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Annual Report 1976

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*Lawrence Berkeley Laboratory
University of California/Berkeley*

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MATERIALS AND MOLECULAR
RESEARCH DIVISION

Annual Report
1976

*Lawrence Berkeley Laboratory
University of California
Berkeley, California*

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VI. APPENDIX

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GENERAL INTRODUCTION

David A. Shirley, Division Head
Rolf H. Muller, Assistant to the Division Head

In 1976 the Materials and Molecular Research Division completed its reorganization and began to reach out in new directions. Division population at the end of 1976 was 51 principal investigators, 118 postdoctorals and other scientific personnel, 278 graduate students, and 79 technical, administrative, and clerical support personnel for a total of 526. The total fiscal year 1977 operating budget was \$8,430,000. During calendar year 1976, 32 Ph.D., 1 Doctor of Engineering, and 25 M.S. degrees were awarded to MMRD students. One hundred and seventy-five journal articles were published by MMRD members during 1976.

Several new projects have gotten underway in MMRD in 1976:

- "The Conversion of Coal to Clean Liquid and Gaseous Fuels" program (Professors Gabor A. Somorjai, Alexis T. Bell, and K. Peter C. Vollhardt) transferred to MMRD from the Energy and Environment Division, adding Professors Bell and Vollhardt to MMRD.
- "Formation of Oxyacids of Sulfur from SO₂" (Professor Robert E. Connick).
- "1.5-MeV Electron Microscopy" (Dr. Kenneth Westmacott). This new project was established to use the new 1.5-MeV electron microscope (expected near the end of 1978) more effectively. This microscope is being funded by the Materials Sciences Office Program, Division of Physical Research, ERDA. It will be managed as a national resource.
- "Excited Quantum Fluids in Solids." Professor Carson D. Jeffries joined MMRD with this project, which was formerly funded independently through ERDA.

The above projects are all funded in ERDA's Division of Physical Research. The following projects are underway in ERDA's applied divisions:

- "Selective Photochemistry" (Professor C. Bradley Moore) and "Isotope Separation" (Professor Yuan T. Lee). Support for these was transferred to the Advanced Isotope Separation Technology Office of the Nuclear Research and Applications Division.

- "Development of Electrochemical Synthesis and Energy Conservation" (Professors Charles W. Tobias, John Newman, and Dr. Rolf Muller). This project is sponsored by the Division of Conservation Research and Technology.

MMRD scientists began substantial projects under the sponsorship of ERDA's Division of Fossil Energy Research. The following projects have been funded:

- "NMR Determination of Coal Composition and Structure" (Professor Alexander Pines).
- "Interfacial Properties of Coal" (Professor Douglas W. Fuerstenau). This project brings Professor Fuerstenau into MMRD.

In July 1976, the ATOM Group (for Advanced Technology of Materials) was established within MMRD, with Professor Victor F. Zackay as Group Leader. ERDA's Administration for Fossil Energy designated this group as a Center of Excellence for materials research. At the end of 1976, the ATOM Group had begun work on the following Fossil Energy projects:

- "Low Alloy Steels for Thick-Wall Pressure Vessels."
- "Wear Resistant Alloys for Coal Handling Equipment."
- "High Temperature Erosion-Corrosion Resistant Materials."

In 1976 MMRD personnel organized several conferences and workshops in Berkeley:

- Fifth International Conference on Atomic Physics, July 26-30, 1976 (Professor Richard A. Marrus).
- Sixth International Materials Symposium: Ceramic Microstructures, August 24-27, 1976 (Professors Richard M. Fulrath and Joseph A. Pask).
- Workshop on High Resolution Electron Microscopy, October 11-13, 1976 (Professor Gareth Thomas and Dr. Robert Sinclair).

●Bay Area Conference on High Temperature Science and Technology, October 16, 1976 (Professor Leo Brewer).

●Workshop on a National Resource for Computation in Chemistry, November 11-12 (Professor William H. Miller).

A number of awards were received by MMRD scientists in 1976:

●*Neil Bartlett* won the coveted Robert A. Welch Award, was made Doctor Honoris Causa by the University of Bordeaux, and received the Alexander von Humbolt "Senior U. S. Scientist" Award, Federal Republic of Germany.

●*Kenneth Pitzer* was awarded the Gold Medal of the American Institute of Chemists and the Willard Gibbs Medal of the American Chemical Society.

●*Bruce Mahan* was elected to the National Academy of Sciences.

●*Joseph Pask* was made an Honorary Life Member of the American Ceramic Society.

●*Charles Tobias* became President-Elect of the International Society of Electrochemistry.

●*Gareth Thomas, Ronald Gronsky, and Robert Sinclair* won the Physical Sciences Prize of the Electron Microscopy Society of America for lattice imaging of alloys.

●*Gabor Somorjai* received the Richard J. Kokes Award of Johns Hopkins University.

●*Marvin Cohen* was named Vice Chairman of the Division of Solid State Physics of the American Physical Society.

●*Donald Olander* received the Division of Materials Science and Technology of the American Nuclear Society Award for his book Fundamental Aspects of Nuclear Reactor Fuel Elements.

●*Alexander Pines* received a Dreyfuss Teacher-Scholar Award.

●*Glenn Seaborg* received the Daniel Webster Award of the International Platform Association for his Charles J. Stroscher Distinguished Scientist Lecture on "The Energy Problem."

●*Marvin Cohen and John (Bill) Morris* were Miller Research Professors.

●*K. Peter Vollhardt* received a Sloan Fellowship for Basic Research.

●*Yuan Lee, William Miller, and Henry Schaefer* received John Simon Guggenheim Fellowships.

The following investigators were made Fellows:

●*Alexander Pines*--Institute of Physics, London.

●*Victor Zackay*--The Metallurgical Society of the American Institute of Mining, Metallurgical and Petroleum Engineers.

●*Gareth Thomas*--American Society for Materials, and Royal Microscopical Society.

●*Yuan Lee and David Shirley*--American Physical Society.

These awards were received in recognition of past achievements. Let's now note briefly a few of the programs under active study in MMRD in 1976:

●*Y. Ron Shen and Yuan Lee* are collaborating on a definitive study of multiphoton dissociation of SF₆ in molecular beams (i.e., under collisionless conditions). This work has already significantly advanced the understanding of multiphoton dissociation.

●*John Clarke* has developed SQUID (Superconducting Quantum Interference Device) circuits that show promise in geothermal exploration. Other possible applications are on earthquake sensors and in magnetocardiology.

●*Kenneth Raymond* is applying "molecular architecture" methods to the development of octadentate anions as specific plutonium sequestering agents for removal of ingested Pu⁴⁺ from the blood.

●*Richard Marrus* is characterizing the lifetimes of transitions in high-stripped ions. These lifetimes have direct application in plasma diagnostics.

●*Alexander Pines* has developed a "double-quantum" nuclear magnetic resonance method that permits the study of spin-one nuclei in solids. It is directly applicable to the study of deuterium in coal.

●*Gabor Somorjai* has organized a surface Science and Catalysis Science Seminar series that brings together investigators from diverse disciplines, to focus on surface and catalysis problems. This seminar series serves as a base on which to build a basic organized interdisciplinary program in this important area.

These are just a few of the current activities that make MMRD an exciting Division. Their scientific quality and technical relevance continue to demonstrate the value of basic research in solving the Nation's energy problems.

David A. Shirley

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I.

Materials Sciences

A. METALLURGY AND CERAMICS

1. HEAVY ELEMENT RESEARCH

a. Microstructure, Properties and Alloy Design

Gareth Thomas, Principal Investigator

Structural Steels

This continuing fundamental program is for investigating the effects of microstructure, especially transformation morphology and retained austenite in quenched and quenched and tempered experimental vacuum melted steels. The objectives are to achieve desirable combination of properties (strength, toughness) economically and without mechanical processing. Practical applications are for high strength, tough steels, e.g., in the mining and transportation industries. The steels are based on Fe/Cr/C.

Duplex Low Carbon Steels

New Fe/Si/C alloys have been designed to produce duplex ferrite-martensite structures by control of composition and heat treatment in the two phase ($\alpha + \gamma$) region followed by quenching. Fundamental studies are continuing to optimize morphological factors, volume fraction of martensite by examining the applicability of the "law of mixtures" developed for composites.

Magnetic Alloys

The principles of spinodal transformations are being applied to a new class of alloys based on Fe-Cr-Co so as to provide good combinations of strength, ductility, and magnetic properties.

Summaries of research programs in the above areas follow.

1. UTILIZATION AND LIMITATIONS OF PHASE TRANSFORMATIONS AND MICROSTRUCTURES IN ALLOY DESIGN FOR STRENGTH AND TOUGHNESS

Gareth Thomas

The development and characterization of microstructures resulting from phase transformations, in martensitic steels and spinodal systems, is outlined and discussed in relation to improvements in ambient temperature strength and toughness. Spinodals and martensites can both have dislocated fine grained microstructures when formed under appropriate conditions. In martensitic steels the importance of retained austenite morphology and stability on toughness at high strengths is emphasized. A method is described for improving the strength of low carbon steels by developing duplex fine grained structures of ferrite and martensite (see

following article no. 3). It is suggested that coarsened spinodal alloys have good work hardening-strengthening potential, if the discontinuous growth problem at grain boundaries can be overcome. Some ideas for the utilization of multiple phase transformations are also presented.

2. IMPROVEMENTS IN STRENGTH AND TOUGHNESS OF Fe/Cr/C STEELS

M. Carlson, B.V.N. Rao and G. Thomas

Previous work has shown how simple heat treatment and control of composition to produce dislocated lath martensite with interlath films of austenite (Fig. 1) lead to extremely attractive combinations of high strength and fracture toughness in an Fe/4Cr/0.35C steel even without tempering. Continuing research has focused upon two areas:

i) Determining the effect of austenitizing temperature upon the microstructure and mechanical properties of the basic Fe/Cr/C alloy;

ii) Improving the strength, toughness, hardenability, and the stability of the austenite by means of quaternary alloy additions.

Influence of Austenitizing Temperature of the Basic Alloy. Test specimens were austenitized over a range of temperatures between 870°C and 1200°C for one hour and quenched in agitated oil. Although the yield and ultimate strengths were unaffected by the austenitizing temperature the toughness and ductility were markedly altered. The fracture toughness, K_{IC} (Fig. 2), increased steadily with austenitizing temperature up to 1100°C, but the Charpy impact energy remained roughly constant (~15 ft/lbs). Slow bend Charpy V-notch tests were performed in order to obtain an "apparent" fracture toughness at failure for a blunt notch show a steady decrease in critical fracture stress and strain with austenitizing temperature.¹ The latter fact is consistent with a decrease in ductility and true fracture stress (from a tensile test) with austenitizing temperature.

Electron microscopy revealed that the primary difference in the microstructure (mainly dislocated martensite) was the undissolved carbide (M_7C_3 type) morphology. At 870°C the carbides were approximately 100Å in diameter and 3μ apart (Fig. 3), increasing the austenitizing temperature to 1000°C and higher resulted in carbides less than 75Å in diameter and spaced greater than 5μ apart.

Fig. 1. Bright and dark field of retained austenite present in as-quenched structure of sample austenitized at 1200°C and oil-quenched. (XBB 765-4568)

Fig. 2. Room temperature toughness properties vs. austenitizing temperature of Fe/Cr/C alloy. (XBL 762-6516)

Fig. 3. Bright and dark field showing undissolved and auto tempered carbides in as-quenched Fe/Cr/C alloy austenitized at 870°C. (XBB 768-7129)

- a. Undissolved Carbides Cr_7C_3
- b. Auto-tempered Carbides Fe_3C

Influence of Quaternary Alloy Additions. The main objectives of quaternary alloy additions to the basic Fe/4Cr/0.3C steel were to improve the toughness and hardenability of the alloy. Mn

Fig. 4. Plot of room temperature fracture toughness vs. yield strength for basic and quaternary alloys. (XBL 764-6733)

Fig. 5. Plot of Charpy impact energy vs. yield strength for the basic and quaternary alloys. (XBL 764-6732)

and Ni were chosen since both elements are known to lower the DBTT and introduce retained austenite in the as-quenched microstructure. The resulting mechanical properties are shown in Figs. 4 and 5. Plane strain fracture toughness, K_{IC} , was superior for all of the quaternary alloys at roughly the same yield strength. The Charpy impact energy of the 2% Mn and 5% Ni alloys were almost 100% greater, at the same strength level. The toughness properties of the Fe-4Cr-2Mn-0.26C steel are far superior to 4340 and 300M at equivalent yield strengths (200 ksi).

1. M. Carlson, B.V.N. Rao, R.O. Ritchie and G. Thomas, Intern. Conf. on Strength of Metals and Alloys, Nancy, France, 2, 509-513, 1976, LBL-5111.

3. DESIGN OF DUPLEX Fe/X/0.1C STEELS: ALLOY DESIGN FOR HIGH STRENGTH LOW CARBON STEELS FOR ENERGY SAVINGS, e.g., AUTOMOBILES

J. Y. Koo and Gareth Thomas

Previous Work. The recent development¹ of duplex ferritic-martensitic structures has offered a wide range of attractive strength and ductility combinations in plain low carbon steels such as 1010 steel. This model system is of interest because the required duplex microstructure can be produced solely by simple heat treatment.

The production of controlled martensite-ferrite microstructure in steels has been described in detail elsewhere.¹ The heat treatment consisted of initial austenitizing treatment followed by annealing in the $(\alpha + \gamma)$ range as shown in Fig. 1. By holding in the two phase range, the α and γ phases will attain the compositions specified by the tie line corresponding to the holding temperature. The alloy will then consist of low carbon ferrite and higher carbon austenite. Upon quenching, the austenite transforms to martensite (strong phase), and the ferrite becomes heavily dislocated due to the $\gamma \rightarrow$ martensite transformation strain.

Current Progress. As a continuing program on the alloy design of low carbon steels, the experimental Fe/C/X alloys (X being varying amounts of Cr and Si) have been investigated with the primary concentration on achieving further improvement in mechanical properties by controlling the morphology and shape of the duplex structures.

From the viewpoint that mechanical properties of two phase materials must be determined by the morphology and properties of the individual phases, a basic approach to obtaining a desirable morphology and shape of the strong martensite phase in a ductile ferrite matrix has been proposed. It is hoped to achieve an optimum com-

bination of strength and ductility by heat treatment alone. The model we adopted is designed according to the theory of fiber strengthening to maximize the potential ductility of the soft phase ferrite and also to fully exploit the strong martensite phase as a load carrying constituent in the duplex microstructure. Table 1

HSLA steels. The attractive properties of the 2%Si duplex steel in comparison with those of the selective commercial HSLA steels are illustrated in Fig. 4.

In addition to the beneficial effect of silicon on the production of ferritic-martensitic struc-

Table 1.

(1) No alloy carbide formers $\therefore$ HSLA not needed

shows the criteria for improved design (specified by General Motors) together with our new results. The arrows show the exciting data.

The tensile properties of the ferritic-martensitic Fe/C/X alloys so far achieved are plotted in Fig. 2. The various properties depending on X are well understood in terms of the proposed model and detailed electron microscopic examinations. The only microstructure which satisfied the proposed model was the one developed in 2%Si steel (Fig. 3). Indeed, the 2%Si duplex alloy exhibited superior strength and elongation ductility combination--better than that of Van 80 which is one of the best available

ture, silicon has further advantages from a practical point of view, as has been recognized in Japan.³

(1) Silicon is one of the alloying elements which open up the ($\alpha + \gamma$) range when added to the Fe-C system so that a wide temperature range in the two phase region is available (Fig. 5).

(2) The fundamental advantages of silicon as an alloying element are that it is inexpensive and readily available.

(3) Silicon is a very effective solid-solution strengthener.

Table 1 shows that the mechanical properties achieved from the new steel (duplex Fe-2%Si -

DUPLEX FERRITE/MARTENSITE STRUCTURES DEVELOPED IN Fe/0.1C/X ALLOYS

OPTICAL MICROGRAPH

Duplex ferrite/martensite structures developed in Fe/0.1C4Cr steel. Globular shape of martensite contrasts with light background ferrite.

Duplex structures developed in Fe/0.1C/0.5Cr steel. Predominantly needle-like martensite is shown within each prior austenite grain. Prior austenite grain boundaries are decorated with continuous martensite phase.

Duplex structures developed in Fe/0.1C/2Si steel show a fine, aligned, and acicular shape of martensite within each prior austenite grain.

Fig. 3

Fig. 1

MECHANICAL PROPERTIES

Depending on the annealing temperature in the $(\alpha + \gamma)$ range, various volume fraction of martensite and a wide range of strength and elongation combinations are obtained.

Fig. 2

Tensile properties of the duplex 2% Si steel are compared with those of commercial HSLA steels.

Fig. 4.

The incorporation of the strong phase martensite as a load carrying constituent in a ductile ferrite matrix can strengthen the composite alloy. The production of such duplex ferrite/martensite structures in Fe/0.1C/X alloys (X being a small amount of a substitutional alloying element) is carried out by an initial austenitizing treatment followed by annealing in the $(\alpha + \gamma)$ with intermediate quenching. Depending on X and the exact heat treatment, various morphologies and shapes of martensite in the ferrite matrix are obtained (Figs. A, B and C) and these seriously affect the corresponding mechanical properties.

A globular shape of the second phase martensite, combined with continuous martensite along the prior austenite grain boundaries (Fig. A), results in relatively poor tensile properties. With microstructures containing a combination of needle-like martensite within each prior austenite grain (Fig. B), while still showing continuous globular martensite along the prior austenite grain boundaries, somewhat improved tensile properties are exhibited. However, upon obtaining a complete needle-like martensite (Fig. C) a superior strength and elongation-ductility combination is found (these properties are compared with those of commercial HSLA steels).

Other factors, such as carbide morphology, solid solution strengthening, etc. were not found to be as significant in determining mechanical properties as the shape and distribution of the martensite phase. Photos were made with polaroid film at 130 X; 2% nital etch.

Figs. 1-4.

(XBB 766-5888)

Fig. 5. Phase diagram showing the expansion of the ($\alpha + \gamma$) range when silicon is added to the Fe-C system. (XBL 761-6344)

0.1%C) already exceed the industrial goals for HSLA steels without the necessity of normal tempering practice. An estimate of weight and fuel savings can now be made. The ranges of weight savings gained by substituting HSLA steels for the current 30,000 psi yield steels are tabulated in Table 2 below:

Table 2. Weight savings potential of HSLA steels.²

Yield Strength	Range of potential weight savings (%)
50,000 psi	22.5 to 40
60,000 psi	29 to 50
70,000 psi	34 to 57.1
80,000 psi	38.8 to 62.5

Table 3 shows the approximate direct worth of a 100 lb weight reduction on fuel economy and performance.

Table 3. Effect of 100 lb weight reduction.²

	Small/Compact cars	Intermediate luxury cars
Fuel economy Effect	+ 0.5 mpg	+ 0.2 mpg
0-10 sec Performance effect	+ 14 ft	+ 7 ft

In conclusion, from the standpoint of the superior properties and simplicity in composition and heat treatment, the new 2%Si duplex steel appears highly promising.

Future work is designed for significant further improvements in properties and a fundamental understanding of their origins. For example, M. Young is also investigating Fe/0.1C and Fe/0.2C steels to evaluate the morphology and applicability of the law of mixtures when applied to duplex alloys in terms of strength and ductility.

1. J. Y. Koo and G. Thomas, Mat. Sci. and Engineering 24, 187 (1976).
2. These data are from the article by D. G. Younger, Manager, Advanced Safety Car Department, Ford Motor Company, Lavonia, Michigan.
3. S. Hayami and T. Furukawa, Micro Alloying, pp. 78-87 (1975).

4. THE MICROSTRUCTURE OF Fe-Cr-Co-Nb-Al PERMANENT MAGNET

M. Okada, M. Homma,* H. Kaneko,* and G. Thomas

Fe-Cr-Co permanent magnet alloys are known to be commercially potential magnets, the energy products of which are comparable to those of Alnico V, with good ductility.¹ It was recently found that the addition of Nb and Al to the Fe-Cr-Co alloy system facilitated heat treatments to produce good magnetic properties.²

The present paper describes the microstructure of an Fe-Cr-Co-Nb-Al permanent magnet. An effect of a thermomagnetic treatment on the microstructures is also discussed since a thermomagnetic treatment plays an important role in producing good magnetic properties in this alloy.

The magnetic hardening of the alloy is performed by tempering after solution treatment. Upon tempering, a α phase spinodally decomposes into two phases, an iron-rich phase (α_1) and a chromium rich phase (α_2).¹

The microstructure shown in Fig. 1 results after the Fe-28wt%Cr-15wt%Co-1wt%Nb alloy is tempered at 640°C for 20 min. The decomposition process appears to be isotropic in the alloy. No satellites are observed in the corresponding diffraction pattern. The decomposed phase (with bright contrast) is identified as iron-rich phase (α_1), approximately 60Å in diameter. Continued aging of the alloy (200 hr) causes the particles to grow (800Å in diameter) as shown in Fig. 2. The growth rate of the particles is described by $\lambda \propto t^{1/2}$.

Figure 3(a) and (b) are the electron micrographs of the alloys tempered at 640°C in a magnetic field of 2 KOe for 5 hr, in planes parallel and perpendicular to the direction of a magnetic field, respectively. The ferromagnetic phase (α_1) has a rod-like shape and is elongated to the direction of the magnetic field, independently of crystal orientation {the region marked A is oriented near (111) and B, (110)}.

Fig. 1. B.F. micrograph showing the decomposition process appears to be isotropic in the alloy tempered for 20 min at 640°C; [100] foil. (XBB 764-3254; left)

Fig. 2. B.F. image showing the coarsened particles after tempering for 200 hr at 640°C; [111] foil. (XBB 764-3254; right)

Fig. 3. B.F. micrograph of alloy tempered for 5 hr at 640°C in a magnetic field of 2 KOe showing the ferromagnetic particles are elongated along the direction of the magnetic field (M), independently of crystal orientation. (a) parallel to magnetic field (M); A: [111] B: [110] orientation, (b) normal to magnetic field [110] foil. (XBB 764-3253)

The ratio of the length to the diameter of the particles increases to approximately 5, which leads to an increase in the shape anisotropy of the single domain.

Our results lead us to conclude that the magnetic properties of the alloy do not depend on the crystal orientation. This is confirmed by the measurement of the magnetic properties of Fe-30wt%Cr-23wt%Co single crystal.⁵

* Department of Materials Science, Tohoku University, Faculty of Engineering, Sendai, Japan.

1. H. Kaneko, M. Homma and K. Nakamura, A.I.P. Conf. Proc., No. 5, 1088 (1971).
2. H. Kaneko, M. Homma, T. Fukunaga, and M. Okada, IEEE Trans. Magnetics, Mag-11, 1440 (1975).
3. H. Kaneko et al., A.I.P. Conf., December (1975), to be published.

b. Ceramic Alloy Program

Gareth Thomas, Principal Investigator

Introduction. The objectives of this program are to obtain a better understanding of defects, phase transitions and relations to properties (physical in the case of the ferrite program, mechanical in the case of refractory carbides and nitrides) by precise applications of electron microscopy. Much basic information is needed as in this regard ceramic systems have been less well studied than metallic systems. We believe such research leads to the possibility of advances in design of ceramic microstructures for improved properties and technical applications.

Transmission electron microscopy has made an impressive impact in ceramics particularly in the ten years that have elapsed since the 1966 Berkeley Conference.¹ There are several reasons why this development has occurred in this time period, e.g., (1) The problem of preparing samples thin enough for electron transmission has been alleviated by advances in techniques, e.g., ion beam thinning and the introduction of high voltage electron microscopes with their greater penetrating power. In 1966 there were no ion thinners or high voltage microscopes in the U.S.A. (2) Many ceramics are beam sensitive, i.e., under electron beam irradiation damage due to inelastic scattering can destroy the specimen through processes such as ionization. This is far more critical than primary knock-on damage. Since the scattering cross sections decrease with energy approximately as $(v/c)^3$ where v is the electron velocity and c is the velocity of light) far less damage occurs to specimens under 1 MeV irradiation compared to say 100 kV (conventional microscopes). This sensitivity to electron beam damage is one of the reasons that MgO has for instance received more attention than the alkali halides. (3) As ceramics generally have complex structures, quantitative microscopy can only be carried out properly when there is adequate theory available for the interpretation of images and diffraction effects. Interest in non-centrosymmetric, anisotropic crystals has now led to the availability of such theories which can provide detailed structural information directly. (4) Recently, advances in high resolution electron microscopy have resulted in intensive research efforts in mineralogy and solid state chemistry in which not only can crystal structure analysis be performed directly from images, but point defects and their mobility can be observed. As an example, resolutions of better than 1 Å were announced in August 1976 by H. Hashimoto² who has successfully resolved the atomic arrangements in a [001] gold crystal. Applications of transmission electron microscopy to current research programs in our group, on ferrites, silicon carbide and silicon nitride, are summarized.

1. "Ceramic Microstructures" edited R. M. Fulrath and J. A. Pask, J. Wiley & Sons, New York, 1968.

2. H. Hashimoto, announced at the Electron Microscope Society of America Conference, Miami, August 8-13, 1976.

a. Absolute Structure Determination

O. Van der Biest*

In addition to the crystal structure imaging methods in which the crystal lattice structure is directly imaged, contrast experiments and the dynamical theory of electron diffraction can be used to provide structure determination. This technique was developed so as to distinguish the two enantiomorphs co-existing in specimens of ordered lithium ferrite.

In general, when the symmetry operations that constitute the space group of a structure do not include either an inversion or a reflection operation, then the structure can exist in two forms, a right-handed and a left-handed one, known as enantiomorphs. When ordered, lithium ferrite can occur in two enantiomorphic forms, $P4_132$ (having a right-handed screw axis) and $P4_332$ (a left-handed screw axis). The presence of the two enantiomorphs co-existing within a sample can be verified in the electron microscope by imaging in dark field in a many-beam orientation with the electron beam parallel to a zone axis, along which the crystal does not show a center of symmetry in projection. Advantage is taken here of violations in Friedel's Law which may cause a difference in background intensity between the two structures. An example is shown in Fig. 1 where many inversion boundaries run through a thick crystal of ordered lithium ferrite and where the enantiomorphs can clearly be seen. When imaged in bright field, the enantiomorphs cannot be distinguished. In order to uniquely identify which regions are of which enantiomorph, care must be taken to correctly index the diffraction pattern so as to establish the unique zone axis. An alternative method, which relies on the difference in intensity profiles for wedge-shaped samples has recently been discussed.¹

It should be stressed that whilst the two enantiomorphs possess distinctly different atomic arrangements it is not possible by standard x-ray diffraction techniques to distinguish between the two.

* Now at Euratom Research Establishment, Petten, The Netherlands.

1. O. Van der Biest and G. Thomas, EMSA Proceedings 1976, Claitor's Publishing Division, Baton Rouge, p. 484.

b. Phase Transitions in Ferrites

O. Van der Biest and R. K. Mishra

We are interested in the ferrites because of their great commercial importance due to their unique magnetic and electronic properties. Both hard and soft ferrites are extensively used in manufacturing microwave device components, computer memory cores and permanent magnets. Ferrimagnetic oxides with the spinel structure

Fig. 1. Multiple beam imaging of inversion boundaries in LiFe_5O_8 . In the dark field image left-handed and right-handed enantiomorphs have opposite contrast. (XBB 766-5394)

form an important class of the ferrites. Conventionally, grain size and porosity have been used for controlling properties in these materials, but it is very likely that heat treatments producing appropriate microstructures could lead to highly desirable properties. Thus, electron microscopy is essential to obtain basic structural information if progress comparable to that made in physical metallurgy is to be made in ceramics. In our continuing program on microstructural characterization in these materials, studies of phase transformation such as ordering and precipitation reactions as well as analysis of defects are being carried out with particular emphasis on lithium ferrite (LiFe_5O_8) spinel.

c. Precipitation Reactions in LiFe_5O_8

R. K. Mishra

In addition to the order-disorder phase transitions at 750°C , lithium ferrite also undergoes a series of precipitation reactions at higher temperatures. This is a common characteristic of many spinel ferrites when held at relatively high temperatures in air and involves a change in stoichiometry due to a loss of oxygen from the structure and a concomitant precipitation of a cation rich phase. This has for instance, been observed in cobalt ferrite, where a wurtzite phase ($\text{CoFe})\text{O}$ precipitates in the spinel phase.¹ In the lithium ferrite, the situation is rather more complicated since at temperatures above 1000°C lithia loss occurs in addition to oxygen loss. This lithia loss phenomenon in fact is one of the major problems in the fabrication of the compound and has up until now limited its widespread utilization. The precipitation reactions studied by HVEM that occur are reported in detail elsewhere,² but the main features are as follows. At short annealing times in air at 1200°C oxygen loss is faster than is lithia loss and a cation rich phase, lithium ferrate, LiFeO_2 forms as small octahedral precipitates dispersed in a spinel matrix (Fig. 2a). The misfit between the two

Fig. 2. Variation of magnetic properties with heat treatment in LiFe_5O_8 . (d) as received; (a) best properties obtained on aging to form coherent lithium ferrate octahedra (A); poor properties (c) are associated with lithia loss (C) on overaging. (XBB 766-5125)

phases is small as both are based on the cubic close packing of oxygen ions; the only difference being in the cation distribution among the interstices. At longer annealing times the particles grow so large ($\sim 2500\text{\AA}$) that they begin to lose coherency by forming interface dislocations with a Burgers vector parallel to $\langle 110 \rangle$ (Fig. 2b).

After prolonged annealing the lithia loss equals the oxygen loss near the edge of a specimen or in a thin sample. Scanning electron microscopy shows that the volatilization of the lithia occurs preferentially at $\{111\}$ planes. This lithia loss causes the LiFeO_2 particles to redissolved leaving behind the interface dislocation network. In a thin sample with a thickness of a few mils, the final microstructure consists of a single spinel phase, but with a high density of dislocations which are the remnants of the intermediate precipitate interface network. In the interior of the bulk samples, however, the two phase microstructure persists. In the later stages of the phase transformation, particles of a glass phase are observed. These are not part of the Li-Fe-O system but rather are actually due to the deliberate incorporation of PbO and B_2O_3 in the preparation of the single crystal used in this work. The magnetic hysteresis properties vary with this precipitation sequence as shown in Fig. 2d. The values of H_C vary with precipitate volume fraction and interface characteristics in an analogous manner to that well known for the yield strength of precipitation strengthened alloys. A dramatic deterioration in magnetic properties occurs due to the lithia loss, whereas the best properties are associated with the presence of a fine dispersion of coherent precipitates of the LiFeO_2 phase (Fig. 2a). Thus these preliminary structure-property results show promise for the eventual production of controlled magnetic properties by the incorporation of a fine dispersion of a nonmagnetic or paramagnetic (e.g., LiFeO_2) phase in a magnetic phase.

1. L. C. deJonghe, Ph.D. thesis, University of California, Berkeley, UCRL-20369.
2. R. K. Mishra, O. Van der Biest and G. Thomas, submitted to J. Am. Ceramic Society.

d. A New Structural Phase Transition in MgAl_2O_4

R. K. Mishra*

In addition to the special diffraction effects mentioned above, electron diffraction itself can provide information on structure at much higher resolution than by x-ray diffraction. For example, many spinel ferrites as well as MgAl_2O_4 spinel have been known to have $\text{Fd}3\text{m}$ space group, as originally determined by Sir W. L. Bragg. However, this has been disputed lately and it has been suggested that the space group of the spinel may be $\text{F}\bar{4}3\text{m}$ one of lower crystallographic symmetry than $\text{Fd}3\text{m}$. In situ electron microscopy and electron diffraction experiments on MgAl_2O_4 spinel show that the space group of MgAl_2O_4 is $\text{F}\bar{4}3\text{m}$ below $\sim 450^\circ\text{C}$. Reflections with $h + k = 4n + 2$, which are not allowed for the $\text{Fd}3\text{m}$ space group appear in the diffraction pattern below this temperature, Fig. 3a. At higher temperatures ($> 450^\circ\text{C}$), these reflections disappear and the space group becomes $\text{Fd}3\text{m}$ (Fig. 3b). Structurally such a transformation corresponds to the displacement of the atoms situated at the octahedral symmetry positions in the high temperature phase to off-center positions in the low temperature phase. On the basis of Landau's

(a)

(b)

Fig. 3. Electron diffraction patterns of MgAl_2O_4 showing change in space group from $\text{F}\bar{4}3\text{m}$ to $\text{Fd}3\text{m}$ upon heating to 450°C .

(a) (XBB 767-5947)
(b) (XBB 767-5946)

theory of second order phase transitions, this transformation could be one of either first or second order. The absence of any observable microstructural changes during the $F43m \rightleftharpoons Fd3m$ transition suggest that this is in fact a second order phase transition.

* LBL-5702, submitted to Acta Crystallographica.

e. Phase Transformation and Polytypism in Silicon Carbide

D. R. Clarke

We have been investigating the detailed microstructure of a recently developed form of high density silicon carbide that shows considerable promise for high temperature structural applications. The silicon carbide, produced by a process invented by General Electric Company¹ in which boron and excess carbon enable pressureless sintering to occur, has a remarkably uniform grain size and is, by x-ray diffraction, composed of the cubic form. However, after the prolonged heating at above about 1800°C in vacuum, exaggerated grain growth occurs and a phase transformation to the hexagonal form occurs. Our current interest is to characterize this sequence of reactions and to describe the mechanisms of the transformations.

The characterization is however complicated by the fact that silicon carbide displays extensive polytypism, so in addition to the basic cubic (β -SiC) and hexagonal (α -SiC) forms there can exist a multitude of possible hexagonal and rhombohedral variants. This can be qualitatively understood from the close packing of nearest neighbor bonded spheres. The crystal structure of silicon carbide may be represented by the close packing of spheres having predominately first neighbor interactions, such that each silicon atom is surrounded by four carbon atoms with a tetrahedral coordination and vice versa. Any observed structure can then be described, by analogy with the close-packed layer stacking in face-centered cubic structures, simply by the stacking sequence of the close packed planes on the three possible stacking positions A, B and C where any one of the three layers actually represents a sheet of silicon atoms and a parallel sheet of carbon atoms. A consequence of the close packing of spheres having nearest neighbor interactions is that the energy of the assembly does not depend on the stacking sequence, and so would result in the case of silicon carbide, of a structure showing complete disordering in one dimension. In general this disordering is not complete however and the stacking sequences exhibit certain preferred periodicities with unit cells having either hexagonal or rhombohedral symmetry. A particularly good example of polytypes is shown in Fig. 4 where the periodicity is 12.6Å, corresponding to five composite Si-C layers, and the symmetry of the unit cell is deduced to be rhombohedral. The polytype is probably 15R.

Fig. 4. Direct superlattice fringe imaging of the 15R polytype in sintered silicon carbide. (XBB 768-6819)

It is in the identification of these stacking sequences that the electron microscope becomes indispensable since they can be present on an extremely fine scale. This is the case in the as sintered General Electric silicon carbide, for although x-ray diffraction indicates that the material is entirely of the cubic form, electron microscopy reveals the presence of numerous regions down to 15.2Å across which have a hexagonal symmetry. These regions are lath shaped, lie parallel to one another on only one of the possible close packed planes and are inside grains that possess an overall cubic symmetry. An example is shown in Fig. 5. This is a [001]

Fig. 5. Coexistence of cubic, twinned cubic and hexagonal variants within a single grain of partially transformed silicon carbide. (XBB 769-8333)

oriented grain and the selected area diffraction patterns taken across the grain demonstrate the co-existence of stacking sequences that have cubic, twinned cubic and hexagonal symmetries.

These mixed stacking sequences, revealed by electron microscopy, are so complex that they cannot all be unambiguously recognized as being polytypes. However, conventional tilting and contrast experiments in the microscope show that these features are associated with a displacement vector of $R = 1/3[111]$ (equivalently $1/6\langle 211 \rangle$) since they become invisible when the specimen is tilted to the $[112]$ pole. An example of such a series of two beam contrast experiments is shown in Fig. 6. Whilst it has not proven possible as yet to determine whether they are produced by deformation or are grown in, they do appear to be either closely spaced stacking faults or micro-twins. From adjacent regions where they are less closely spaced, the formation of a conventional twinned diffraction pattern suggests strongly that they are indeed micro-twins.

The presence of hexagonal regions within the cubic grains of the as-sintered compacts has important implications for the transformation mechanism to the final hexagonal form. For this reason we have been applying direct lattice imaging and the recently developed technique of optical microdiffraction from the lattice image² to obtain quantitative information on the distribution of stacking sequences. Preliminary optical micro-diffraction measurements have been reported,³ so only the lattice imaging results will be described here. The lattice fringe technique in the electron microscope makes it possible to observe the stacking of the close packed planes directly. An example of this is given in Fig. 7 where one set of close packed planes, spacing $2.52\text{\AA}$, can be clearly seen. In addition, the dark and rather diffuse lines

Fig. 6. A series of micrographs taken under different diffraction conditions showing that the complex stacking sequences in silicon carbide are associated with a displacement vector of $R = 1/3[111]$.
(XBB 767-6521)

Fig. 7. High resolution dark field electron micrograph illustrating the intergrowth of cubic (β) regions with single polytype regions designated by their polytype notation.

(XBB 768-6628)

delineate the stacking sequences; these are the lines that are usually seen in the lower resolution images such as in Fig. 4. On the figure the probable polytype designations have been marked and the spatial complexity of the transformation becomes apparent since some of the polytypes are only one unit cell wide and are surrounded on either side by untransformed cubic phase. Obviously, this type of local crystallographic information can only be obtained by using high resolution electron microscopy.

The next step in understanding the transformation is to observe and identify the faults responsible for the conversion from the cubic structure to one of the hexagonal forms. Whilst this remains to be done there are indications that such transformation faults do indeed exist. These faults are quite elusive and it has not so far been possible to unambiguously characterize them.

Another striking feature of the microstructure of silicon carbide is the exaggerated grain growth that occurs on annealing above about 1800°C. Since the final microstructure of the silicon carbide consists of long tabular shaped grains of hexagonal structure all the electron microscope observations can be rationalized by assuming that there are essentially two simultaneous processes occurring on heating. Firstly, there is a grain growth process which is unusual in that the growth only occurs on one of the possible close packed planes, and secondly there is the concomitant transformation from cubic stacking to hexagonal stacking by a twinning or faulting mechanism. In this particular form of silicon carbide the crystal structure transformation is slower than the exaggerated grain growth.

Investigation of Grain Boundaries. In many ceramics the properties, particularly the mechanical properties, are determined by their

grain boundaries. This is especially true for the creep properties and the loss of high-temperature strength. The grain boundary regions are of further importance since most ceramics are formed by either sintering or hot pressing, both of which depend critically on the properties of the grain surfaces and boundaries. Clearly, then, their characterization in ceramics is extremely important and electron microscopy is just beginning to be brought to bear on this problem by direct lattice imaging of the crystal planes on either side of the boundary. This is a new technique and early results are discussed in the next section.

f. Lattice Imaging of Grain Boundaries Silicon Nitride*

D. R. Clarke

The investigation of the grain boundaries in silicon nitride is of particular importance at the present time because of the intensive effort in the U.S.A. U.K., Germany and Japan, to demonstrate that silicon nitride can truly be a structurally important high temperature material. One of the major problems preventing its application is the rather dramatic decrease in the strength and toughness of the hot pressed form above about 1000°C. This decrease is generally attributed to the presence of a glassy phase, between the individual silicon nitride grains, which at high temperatures rapidly decreases in viscosity with temperature, flows and allows the grains of silicon nitride to slide past one another. Whilst this model is extremely attractive and the available experimental evidence appears to support the model, no direct observation of a glassy phase between the boundaries has been made. We have tackled this problem by imaging directly the crystal lattice planes up to, and on either side of selected grain boundaries in a 5% MgO hot pressed silicon nitride. The technique used is that of lattice fringe imaging, which has already proved to be extremely valuable in investigating phase transformations in metallic alloys and the structure of a variety of minerals.

Figure 8 is of a high angle boundary between two alpha silicon nitride grains, looking almost straight down the boundary plane. The lattice fringes can be followed right up to the boundary from either side demonstrating the absence of any intergranular amorphous layer. A further striking feature of the micrograph is the straightness and smoothness of the boundary plane which suggests that the surface energy of α -silicon nitride is highly anisotropic.

Since these lattice images and those from many other high angle boundaries indicate the absence of any amorphous or glassy layer between two adjacent grains, the problem arises as to where it is in the microstructure. The evidence that a glassy phase does exist is extremely persuasive and we have evidence for its existence only at triple point grain boundary junctions e.g., Fig. 9.

Work is now proceeding to apply these techniques to silicon ceramics (T. Shaw and D. R. Clarke).

Fig. 8. A high angle grain boundary between two α -silicon nitride grains. The presence of lattice fringes right up to the boundary on either side confirms the absence of any amorphous grain boundary phase. (XBB 767-6448)

Fig. 9. A triple point, A, revealed by lattice fringe imaging of the surrounding α -silicon nitride grains. The lack of diffraction contrast on tilting indicates that the triple point contains a glassy phase. (XBB 769-8516)

* Supported by NSF.

1. S. Prochazka and P. C. Smith, General Electric Report 74CRD040, April 1976.
2. R. Sinclair, R. Gronsky, and G. Thomas, Acta Met. 24, 784 (1976).
3. D. R. Clarke and G. Thomas, Proc. 34th EMSA Conf., Miami Beach, Florida, Claitor's Publishing Division, Baton Rouge, p. 492.

c. High Resolution, and High Voltage Electron Microscopy

Gareth Thomas, Principal Investigator

1. PRESENT STATUS OF HIGH RESOLUTION STUDIES AT BERKELEY

Gareth Thomas

In a structural approach to understanding materials at the atomic level, there are four important parameters about which we need information. These are:

- (i) atomic identity;
- (ii) atomic coordination;
- (iii) atomic environment;
- (iv) deviations from perfect crystallinity near lattice defects.

At present, the resolution limits of current transmission electron microscopes is $3.5\text{\AA}$ point-to-point and $2\text{\AA}$ line.¹ We are not able to achieve atomic resolution and identification in most materials, particularly those with close-packed structures such as metals. The aim of a complete atomic description of materials is thus not yet possible. However, with the slightly lower resolution available, lattice fringe imaging is feasible and from these images we can obtain the following information:

- (i) localized crystalline structure;
- (ii) localized chemical composition;
- (iii) configuration and role of lattice defects.

Such information is not generally available from conventional bright and dark field images. It is our experience that the detail revealed by fringe imaging is considerable when compared with conventional imaging modes. It is to be expected that the logical step to atomic resolution will also open up hitherto unforeseen data. Here we summarize recent results obtained in our group by lattice imaging, the benefits and limitations of these images, and the possibilities that may arise from atomic resolution at the sub $2\text{\AA}$ level. The work in ceramics is described in the previous section.

Current Applications and Limitations. Most structural alloys in service are utilized in a highly defective condition, having undergone partial transformation from an unstable to stable, or metastable, form. Phase transformations are therefore central to alloy development and design and much of our work has gone into understanding the associated atomic mechanisms.²

In ordering and martensitic reactions, changes in crystal structure occur without change in composition. Thus we are investigating the first and third factors described above. The structural changes occurring in ordered alloys are revealed by changes in fringe profile, from that of the fundamental lattice to that of the superlattice. During martensitic reactions we observe the change of fringe orientation and spacing. We have new data on the nature of short-range order, the structure of lattice defects such as anti-

phase boundaries, rotational domain boundaries and superdislocations, the nature of the order-disorder interface and the austenite-martensite interface, and the initial nucleation stages of ordering. Features such as interface ledges, e.g. Fig. 1, dislocations and degree of order

Fig. 1. Unit cell ($5.3\text{\AA}$) high steps are indicated in the interface between two domains in fully ordered Mg_3Cd . It is thought that they provide the mechanism (ledge) for domain growth in this alloy although in situ high resolution hot stage experiments (not possible with current instrumentation) would be necessary to conclusively establish this point. These features cannot be detected in conventional TEM images. (XBB 766-5696A)

variations are readily revealed. However, in seeking the atomic environment, we are limited to profiles in one dimension only and formed from a column of atoms. Thus we are still averaging over 10 to 1000 atoms to provide local values for degrees of order. For ultimate information on the atomic environment, we need interpretable point resolution of $2\text{\AA}$ (or better).

During spinodal decomposition there is no structural change, only highly localized fluctuations in composition. Using fringe images these can be established from the relationship between interplanar spacing and composition. By averaging over five fringes we can obtain about 1% precision³ and thus detect small compositional changes on a $10\text{\AA}$ level. If resolution is sacrificed higher accuracy can be achieved and Wu has been able to plot the d-spacing profile even in Cu-Ni-Cr in which the maximum difference in lattice spacing is only 1% (Fig. 2).

However, these studies rely both on ignoring the effects of localized strain effects and on assuming a one-to-one correspondence between fringes and lattice planes. More sophisticated theoretical calculations are required to assess the importance of these assumptions. Nevertheless, there is little doubt from optical diffraction analysis and complementary conventional electron microscopy, that the variations in d-spacing detected in the image are related to the microstructure of the material.³ More detailed

Fig. 2. Plot of {200} interplanar spacing with distance along the $\langle 100 \rangle$ direction in spinodally decomposed Cu-Ni-Cr. The wavelike d-spacing variations are due to the composition modulations of transformation, and are revealed directly, for the first time, by lattice imaging.

(XBL 769-7491)

analysis of spinodal alloys than is possible from fringe images must await higher resolution instruments.

The role of the lattice defects is particularly important in discontinuous precipitation reactions. Here one of the greatest problems is the experimental expertise required to image simultaneously both the produce precipitate phase and the two matrix grains on either side of the

Fig. 3. A low magnification view of the discontinuous precipitation reaction in Al-Zn. The participating phases are clearly distinguishable with the precipitate central, the grain into which it is growing upper right, and the grain left behind in the lower left of the picture.

(XBB 767-6527)

Fig. 4. High magnification views of the areas marked in Fig. 3, showing the fine structure of the precipitate-matrix interface. Atomic spacing ledges are indicated which are not resolved in the conventional micrographs, and which are thought to be important in the mechanism of the phase transformation.

(XBB 767-6528)

moving grain boundary and this severely limits the imaging success rate. The studies of Gronsky² (Research supported by NSF) have detected unit cell ledges in faceted particle-matrix interfaces (Figs. 3 and 4), the presence of misfit dislocations and the existence of a transition region between the parent and product phases in certain alloy compositions. Ultimately, one would aim for identification of individual species and their location with respect to the grain boundary, which is not possible currently. Internal interfaces, e.g., non-conservative antiphase boundaries can also be imaged to show composition changes (indirectly) through fringe spacings.

Current Status and Future Directions. Although we are obtaining considerably more information from lattice images than from conventional micrographs there are still a number of problems preventing us from attaining our goal of atomic resolution and identification. The resolution of conventional 100 kV instruments is limited. The thickness of specimens for image interpretation in terms of projected charge density must be less than 100 Å, which is generally not possible for many materials. Both these factors can be overcome by utilizing higher voltage, high resolution instruments. Voltage increase also improves the possibility of studying beam-sensitive materials such as polymers and biological specimens. The interpretation of high resolution images, particularly for the imperfect lattices which are often encountered in practical materials, requires more sophisticated theories than currently used. Image formation is still not experimentally routine and the output of lattice images is low when compared to conventional images. Again this situation should improve with better instrumentation. Specimen stages for *in situ* experiments (e.g., heating, cooling, environmental) are far below even lattice fringe resolution. It is to be expected that much more reliable conclusions

can be drawn about materials behavior by actually observing reactions at the atomic level as they occur.

All areas of materials science should profit by atomic resolution, but perhaps the most dramatic development can be in the radiation damage field. To image point defects (interstitials and vacancies), identify the environment in which they exist and observe their migration in various materials would considerably enhance our understanding of this important phenomenon. Such experiments should be feasible in a 2Å point resolution, high voltage electron microscope, equipped with a high resolution cold stage.

One final point that must be considered is that there is a feeling of excitement in electron microscopy now that we are on the verge of atomic resolution. These results, coupled with the fact that despite the limitations on selected area diffraction due to electron optical errors (spherical aberration) which can be overcome, at least geometrically, by utilizing optical microdiffraction,⁵ indicate unlimited potential for HREM. Further improvements in instrumentation, e.g., beam source, lens aberrations, which will also yield higher diffraction and spectroscopic resolution, can in the final analysis lead to the ultimate goal as iterated in the introduction viz., atomic resolution and identification. These factors are reiterated in the summary report of the HREM Workshop given below.

1. J. M. Cowley, Ann. Rev. Mats. Sci. 6, 53 (1976).
2. G. Thomas, R. Sinclair, and R. Gronsky, Proc. 6th European Congress on Electron Microscopy 1, 114 (1976).
3. R. Sinclair, R. Gronsky, and G. Thomas, Acta Met. 24, 789 (1976).

2. WORKSHOP ON HIGH RESOLUTION ELECTRON MICROSCOPY* (Oct. 11-13, 1976)

Gareth Thomas

Electron Microscopy at Atomic Resolution

The resolution and unique identification of individual atoms and point defects and their environment is itself a unique scientific achievement.

In order to accomplish this, however, it will be necessary to obtain one of a new generation of high voltage electron microscopes requiring a substantial capital investment.

The use of such a high voltage high resolution electron microscope (500 kV, 1.7Å point-to-point) can give an improvement in resolution by a factor of two, relative to present instruments, for images which can be interpreted directly in terms of atom positions. This will take us past a critical barrier (2Å) the interatomic distance in solids, and open up the entire field of study

of atomic configurations, and consequently many fields of research, since information will be obtained which is hitherto unavailable. Convenience and versatility of observations will be enhanced by the increase by a factor of 3 or 4 in specimen thickness for directly interpretable images compared to 100 kV instruments. The image contrast for individual atoms or atomic defects in crystals will be enhanced by a factor of 2 or 3. These trends are shown graphically in Figs. 1(A)-(C) demonstrating that high voltage

Fig. 1. (A) Plot showing enhancement of resolution with increasing accelerating voltage for conditions of constant $C_s\lambda$ and constant C_s . (B) Graph of thickness vs. voltage indicating realm of validity for the phase object approximation. The possibility of directly interpretable images of atom arrangements is implied. (C) Contrast for single atoms or atomic defects in crystals as a function of accelerating voltage under constant resolution, constant $C_s\lambda$ and constant C_s conditions. Solid lines indicate a point-like representation of atoms, dotted lines account for the effect of finite atom size. (Courtesy J. M. Cowley)

[(A & B) XBL 773-7921; (C) XBL 773-7921]]

electron microscopy is essential for atomic resolution and interpretation. In addition, the reduction of bond-breaking damage due to inelastic scattering which decreases as the cube of the electron velocity gives an added advantage of 500 kV HREM (a factor of 4) over 100 kV for the study of beam sensitive materials (polymers, ionic crystals, biological, etc.) at atomic resolution.

The workshop report^{*} discusses in detail the many facets of microscopy at atomic resolution including theory, instrumentation, many potential fields of application and the need for a National Facility to accomplish the goals. The workshop report is itself preceded in the following by a summary section in which the organizing committee point to many examples of scientific applications and potential new achievements which become possible when an atomic resolution microscope is available to a term of researchers.

Summary of Some Expected Scientific Benefits

The Organizing Committee[†]

The achievement of interpretable resolution of structure at the atomic level, itself a major breakthrough in science, opens up many new and exciting avenues of research, and the workshop report itself discusses many examples. Here, the organizing committee draws attention to these and Fig. 2 summarizes some specific research projects envisaged for a HREM center at Berkeley.

It is not impossible that we may even be able to study atomic motion directly, i.e., observe dynamic events at atomic resolution in the microscope. What enormous possibilities this concept conjures up.

Point Defects: Impurities

- Mechanisms of transport; diffusion
- Physics of electrical, optical and thermal behavior
- Radiation damage; swelling: implications to reactors
- Ionic Conduction--power storage cells
- Atomic configurations at defects:
 - Dislocations
 - Interactions: dislocations - point defects and impurities: segregation
 - Mechanical properties especially creep, fatigue
 - Heterogeneous phase transitions

Surfaces

- Catalysis
 - Local atomic configurations
 - Nucleation, growth mechanisms
 - Poisoning mechanisms
- Oxidation
 - Transport mechanisms, growth
- Reduction
 - Mechanisms; mineral processing and extractive metallurgy

Corrosion

- Initiation sites
- Influence of defects

Crystalline Materials (metals, alloys, minerals, ceramics, and compounds)

- Real Space Crystallography
 - Structure analysis
 - Identification of cations
 - Short range order
- Geology - high pressure phases, relation to seismic properties of earth's deep mantle:
 - History and physical properties of our parent planet
- Solute atom distributions
 - Mechanisms of phase transitions
 - Interstitial solutes: ordering; steels
 - Segregation to defects; interactions
 - Embrittlement
- Martensitic Transitions
 - Identification of nucleation events
 - Interfacial structures
- Internal Surfaces
 - Structure and properties of boundaries
 - Grain boundary segregates: phases
 - Ceramic interfaces, porosity
 - Interphase interfaces
 - Quantitative characterization of interfacial defects; solute interactions

Amorphous Materials

- Structure Analysis in real space
 - Resolution of whether amorphous materials are amorphous - correlation to radial distribution functions
 - Structure - property relations
 - Metals, semiconductors

Polymers and Glasses

- Structure Analysis in real space
 - Investigations of inhomogeneities
 - Glass Ceramics; phase transitions
 - Crystalline polymers: nucleation of spherulites; growth mechanisms
 - Effects of local epitaxy

Biology

- Principles of Molecular Structure
 - Cell membranes
 - Cell functions
 - Natural protein structure
 - Nucleic acid sequencing
 - Biomedical engineering

^{*} Complete Workshop Report appears as LBL-5722.

[†] Report of the Organizing Committee: J. M. Cowley, R. M. Glaeser, R. Sinclair and G. Thomas.

HIGH RESOLUTION ELECTRON MICROSCOPE FACILITY

Objective:

NEW DISCOVERIES ON THE STRUCTURE OF MATTER BY DIRECT OBSERVATIONS AT THE ATOMIC AND MOLECULAR LEVEL

Fig. 2. High resolution electron microscope facility.
(XBL 771-50)

3: HIGH VOLTAGE ELECTRON MICROSCOPY OF DEFECTS IN LITHIUM FERRITE SPINEL

R. K. Mishra*

Ferrimagnetic oxide spinels are an important class of modern technological ceramic materials. These have long been recognized as being predominantly ionic in nature. Hornstra's¹ crystallographic study of planar and line defects in spinel structure shows that dislocations of Burgers vector $1/2 \langle 110 \rangle$ can dissociate into two partials $1/2 \langle 110 \rangle = 1/4 \langle 110 \rangle + 1/4 \langle 110 \rangle$ bounding a cation stacking fault on $\{111\}$ glide planes. These partials, in turn, can dissociate into quarter partials of Burgers vector $1/12 \langle 112 \rangle$ on $\{111\}$ planes, reducing strain energy and at the same time preserving electro-neutrality

through a synchroshear mechanism. The current paper describes experimental studies on the nature of the glide dislocations and their dissociation in lithium ferrite (inverse spinel) using high voltage transmission electron microscopy. High order bright field² electron micrographs taken in the HVEM together with the computed image profiles implementing multibeam dynamical theory are used to determine the fault plane and estimate the stacking fault energy.

Glissile dislocations are introduced by plastically deforming single crystal specimens at high temperature (1200°C). Thin foils for examination in the microscope are prepared from these specimens by mechanical thinning followed by ion bombardment. The foils are examined in the Hitachi HU-650 electron microscope operating at

Fig. 1. Dislocation networks in plastically deformed LiFe_5O_8 . Foil orientation near (110) . The operating reflection is indicated (actually imaged in ng). (XBB 764-3091)

650 kV. Figure 1(a) and 1(b) show dislocation networks in a particularly thick ($>5\xi_g$) region of the specimen under different diffracting conditions. The Burgers vectors of the total and partial dislocations are determined from diffraction contrast experiments. The results show that almost all dislocations are dissociated according to the reaction $1/2 \langle 110 \rangle = 1/4 \langle 110 \rangle + 1/4 \langle 110 \rangle$. Determination of the fault plane is less direct due to absence of stacking fault fringes ($\xi_g \approx 10^3 \text{Å}$) and is done from geometrical considerations. From the micrographs, it is seen that the images are parallel to the intersection of the $\{011\}$ planes with the specific foil plane (110) . This result has been confirmed by examination of

dislocations in a large number of foils in different orientations. No dislocations on $\{111\}$ planes have been found in LiFe_5O_8 in the entire course of this investigation contrary to Hornstra's analysis and some reported observations in MgAl_2O_4 .

Figure 2(a) shows dissociated dislocations imaged with $s_{4g} = 0$. Figure 2(b) and 2(c) are the microdensitometer trace at A and the corresponding computed image profile respectively. Dislocation A is a mixed dislocation of total Burgers vector $1/2[011]$. The dissociation can be represented as $1/2[011] = 1/4[011] + 1/4[011]$ on the $(01\bar{1})$ plane connected by a cation stacking fault. The average value of the nonconstricted part of the extended dislocations is measured to be $(150 \pm 20 \text{Å})$ from microdensitometer traces. This corresponds to a stacking fault about 220Å wide in the cation sublattice on the $(01\bar{1})$ plane. The stacking fault energy can then be calculated from the theory of dislocations. In the anisotropic case, the value determined is 75 ergs/cm^2 . It may be remarked that although the value of γ reported here seems relatively low for an ionic compound, this agrees well with the calculated value of γ for LiFe_5O_8 .⁴

* EMSA Student Fellowship Award 1976.

1. J. Hornstra, Proc. of the 4th International Conf. on Reactivity of Solids, Elsevier, Amsterdam, 1961, p. 563.
2. W. L. Bell and G. Thomas, Electron Microscopy and Structure of Materials, University of California Press, Berkeley, 1972, p. 23.
3. G. Welsch, et al, Philosophical Magazine 29, 1371 (1974).
4. R. K. Mishra, unpublished research.

Fig. 2. (a) Dissociated dislocations in LiFe_5O_8 imaged near the (110) pole. (b) Microdensitometer trace at A. (c) Computer profile for $1/2[011] = 1/4[011] + 1/4[011]$ (8 beam systematic $\langle 220 \rangle$). Excellent agreement exists between theory and experiment. (XBB 758-5877)

4. PRELIMINARY OBSERVATIONS OF ELECTRON IRRADIATION DAMAGE IN SHORT-RANGE ORDER Ni_4Mo

R. Sinclair, D. S. Gelles,* and G. Thomas

Short-range order (SRO) in a solid solution is an inherently stable state. It is a highly localized phenomenon, with atomic correlations rarely extending more than a few unit cells and which is difficult to study and interpret by conventional methods. It has been invoked as one of the possible causes of low swelling rates during irradiation of specific alloys.¹ This idea is currently gaining some foundation especially as swelling has been found to be low in Cu 15%Al² and Ni_4Mo ,³ both of which are well-known SRO alloys.^{4,5}

The present experiments are aimed at evaluating the behavior of SRO Ni_4Mo (produced by quenching from above the critical ordering temperature) in an irradiation environment. For this purpose, thin foils, prepared by electropolishing 3 mm disks in dilute H_2SO_4 at room temperature, were examined in a JEOL high voltage electron microscope operating at 1 MeV (i.e., above the threshold displacement energy for both Ni and Mo). The temperature of the irradiated area was estimated to be 100°C, from the known temperature rise caused by the focused electron beam in this microscope.⁶ The variation of selected area electron diffraction patterns was recorded during irradiation and dark field micrographs were taken in and near to the irradiated area.

SRO in Ni_4Mo is manifested by weak diffuse scattering at $\{1\frac{1}{2}0\}$ positions in diffraction patterns. A $[112]$ zone illustrates this feature.

Little variation was found in the intensity of the diffuse reflections upon irradiation of the sample in this orientation, up to a dose of five displacements per atom (Fig. 1). Any change occurred in the direction of increased $\{1\frac{1}{2}0\}$ intensity. Thus SRO is indicated to be stable by the diffraction patterns. It seems significant that SRO was not destroyed by irradiation (disappearance of $\{1\frac{1}{2}0\}$ spots) nor that long-range ordering was induced (as would be revealed by the appearance of long-range order reflections at $\{\frac{4}{5}\frac{2}{5}0\}$ positions).

Dark field micrographs taken using $\{1\frac{1}{2}0\}$ reflections are shown in Fig. 2. In the unirradiated area (Fig. 2a) the tiny ($\sim 10\text{\AA}$) microdomains, which characterize SRO in this material and which are extremely difficult to image,⁷ are unresolved. In the irradiated area the image resolved ordered domains (Fig. 2b), indicating that the nature of SRO has indeed changed during irradiation, with the production of larger microdomains.

This experiment shows that SRO in Ni_4Mo is not destroyed by electron irradiation up to 5 d.p.a., but indicates that domain coarsening may occur. Clearly this result is of considerable interest in assessing the effect of radiation damage on the fine structure of alloys, and vice versa, and that further characterization of this reaction is desirable.

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Fig. 1. $[112]$ electron diffraction patterns of SRO Ni_4Mo after (a) 0.25 d.p.a. (b) 2.5 d.p.a. by 1 MeV electron irradiation.

[(a) XBB 763-2690A; (b) XBB 763-2691]

Fig. 2. $\{1\frac{1}{2}0\}$ dark-field micrographs of Ni_4Mo (a) unirradiated, (b) irradiated to 5 d.p.a. (XBB 763-2748)

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5. STUDIES OF ATOMIC SCATTERING FACTORS FROM THE CRITICAL VOLTAGE OF ORDERED ALLOYS--APPLICATION TO Cu_3Au

A. Rocher, R. Sinclair and G. Thomas

The critical voltage effect, first discovered by Uyeda,¹ and Nagata and Fukuhara,² has been already used to determine the experimental values of the Atomic Scattering Factor.³ The technique developed by Rocher and Jouffrey³ is applied to ordered alloys. The main interest of this study is to yield complementary information about ASF for pure metals and Debye temperature for alloys.

For ordered alloys the 100 and 110 reflections are allowed. Then there are interactions potentials V_{100} and V_{110} , perturbing the dynamical effects such as critical voltage. It is then possible to determine the values of V_{100} and V_{110} potentials as a function of critical voltage.

Methods of Calculation

Two eigenvalues of the fundamental equation are equal at the critical voltage. This fact has been used for the calculation of a criterion for the determination of the critical voltage.

The difference between the two eigenvalues equal at the critical voltage is to a first

approximation a linear function of the accelerating voltage. The precision of the calculation has been limited to one kilovolt. Indeed the experimental results are always bigger than a few kilovolts. In addition the computation times are reasonable with about five iterations from the three beam calculated critical voltage.

Critical voltages are calculated with a limited number of parameters. Compared with the experimental values (least square method), they permit the determination of the real values of the ASF by an atom in pure metals and the Debye temperature of an alloy.

Choice of Parameters

a. Atomic Scattering Factor. Thomas et al.⁴ showed that the Doyle and Turner⁵ ASF in gold yields calculated critical voltages very close to the experimental results for angles larger or equal to that for the 200 reflection.

The experimental values of the copper ASF are given by Rocher and Jouffrey for reflections larger or equal to that for the 111 reflection.

The ASF of alloys are calculated with the assumption that the A atom in the pure metal and the A atom in the A_nB_{1-n} alloy have the same ASF. Then for Cu_3Au ASF F_g are correctly determined from ASF values known for copper and gold. In the formulation used by Doyle and Turner:

$$F_g = \sum_{i=1,4} A_i \exp - B_i g^2. \quad (1)$$

The last three terms, giving the variation for the large angles, can be considered as correct. For copper and gold the first term only should be corrected in order to yield good agreement between experimental values and calculated values of the critical voltage for fully ordered alloys.

b. Debye Temperature. Shirley et al.⁶ give an equation to define the Debye temperature of an alloy, θ , which is a function of the mole fractions m_A and m_B of A and B atoms, μ_A and μ_B their atomic weight and θ_A and θ_B their pure metal Debye temperatures. The relation is written:

$$(m_A \mu_A + m_B \mu_B) \theta^2 = m_A \mu_A \theta_A^2 + m_B \mu_B \theta_B^2 + (z-1)(1-\alpha) m_A m_B (\mu_A \theta_A^2 + \mu_B \theta_B^2) \quad (2)$$

where α is the nearest neighbor Cowley Warren⁷ short range order parameter and τ is a characteristic constant of the interatomic forces. This parameter is determined by critical voltage method.

Results

The experimental results used in this paper are given by Thomas et al. and by Sinclair et al.⁸ (Table 1). Not very accurate measurements of the 440 critical voltage can be obtained because of the high irradiation rates at ≈ 1400 kV. Therefore we can only verify that the experimental values are comparable with the calculated values.

Table 1.

		Thomas et al.	Sinclair et al.	Calculation
$\alpha = 1$	222	175 $\pm$ 3 kV		175 $\pm$ 2 kV
$\theta = 261$ K	400	425 $\pm$ 3 kV	429 $\pm$ 10 kV	422 $\pm$ 3 kV
$T = 293$ K	400 (T = 461 K)	364 $\pm$ 3 kV		363 $\pm$ 3 kV
	440		> 1400 kV	1.470 $\pm$ 10 kV
$\alpha = 0$	222	166 $\pm$ 3 kV		166 $\pm$ 2 kV
$\theta = 193$ K	400	381 $\pm$ 3 kV	360 $\pm$ 10 kV	381 $\pm$ 3 kV
$T = 293$ K	440		≈ 1300 kV	1.285 $\pm$ 10 kV

The ordered alloy permits the determination of A_1 coefficient for copper and gold. Indeed $\alpha = 1$ and the Debye temperature is well known with the Eq. (2) and macroscopic data.

A_1 (Cu) and A_1 (Au) have been determined with two 400 critical voltages taken at two different temperatures and the 222 critical voltage has been used as a check (see Table 2).

The 222 critical voltages vary with the degree of order. This effect cannot be explained by a variation of ASF, which is the same for the ordered alloy and the disordered alloy. This effect can be well explained by the variation of the Debye temperature of Cu₃Au given by Eq. (2). The coefficient τ is determined in disordered Cu₃Au alloy ($\alpha = 0$) with the 222 and 400 critical voltages: $\tau = 0.7 \pm 0.04$. This value can be compared with these given for FeCr by Shirley et al.

Table 2.

	A_1	V_{100}	V_{200}
Cu	2.75 $\pm$ 0.1 Å	18.5 $\pm$ 0.2 V	11.00 $\pm$ 0.05 V
Au	2.15 $\pm$ 0.2 Å	24.4 $\pm$ 0.4 V	17.25 $\pm$ 0.05 V

All the critical voltages calculated from the parameters thus determined fall within experimental errors.

The uncertainties in the calculated critical voltages result from uncertainties in the determination of the parameters taking experimental errors into account.

In conclusion, we have confirmed that the ASF of an atom within the gold lattice and that of a single gold atom have almost the same values. Conversely for copper the scattering by a free atom and the scattering by an atom within the crystal are quite different. The question is to know whether the assumptions made in the Hartree Fock method are reliable or not, or to know the influence of the lattice on the scattering by single atom.

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6. CLIMB AND GLIDE DISLOCATION SOURCES IN QUENCHED ALUMINUM ALLOYS

K. H. Westmacott

Concentric dislocation loops are observed frequently in slowly quenched aluminum alloys (for a review see Ref. 1). In Al-Cu alloys containing Si as an impurity the loops are found to lie in $\{111\}$ planes in configurations that have been inferred to arise from the operation of Frank-Read glide sources. On the other hand, in Al-Mg and Al-Si alloys detailed analysis has shown that the loops form by dislocation climb in the manner proposed by Bardeen and Herring. Recent work has shown that all multiple loop configurations in Al and its alloys have a common origin, and result from dislocation nucleation and/or vacancy condensation in the vicinity of inclusion particles.² These processes occur to relieve the large compressive strains which are generated in the lattice around the misfitting particle. It is not clear, however, under what

specific conditions the various processes, i.e., vacancy condensation, glide or climb loop generation, will operate. In this paper it is shown that in Al-Si both climb and glide loops can be produced concurrently.

The alloy used in the experiment contained 0.67w/oSi and was quenched into silicone oil at 100° C after a solution treatment at 550° C. Samples for study in the Philips EM 301 were prepared by a chemical polishing techniques to eliminate mishandling damage.

The samples contained high concentrations of multiple loops which analysis has shown arise from the operation of climb sources.² In one instance, however, the detailed contrast analysis (see Figs. 1-4) revealed exceptional behavior. The loop Burgers vectors $\vec{b}$ were determined in the standard manner by setting up two-beam conditions for various diffraction vectors, $\vec{g}$. In Figs. 1-3 the electron beam direction, B , was $[111]$, and the effect of varying $\vec{g}$ is shown. In Fig. 4, $B = [121]$

Fig. 1. $B = [111]$ $\vec{g} = [\bar{2}20]$.

Fig. 2. $B = [111]$ $\vec{g} = [\bar{2}02]$

Fig. 3. $B = [111]$ $\vec{g} = [0\bar{2}2]$.

Fig. 4. $B = [121]$ $\vec{g} = [\bar{1}1\bar{1}]$.

and $g = [\bar{1}1\bar{1}]$. The dislocation visibility in each condition is summarized in Table 1, while Table 2 shows the possible $|g \cdot b|$ values for vacancy loops with $[\bar{1}\bar{1}\bar{1}]$ plane normals.

A comparison shows that for both outer loops $b = \pm 1/2[\bar{1}01]$ i.e., they are glide loops, whereas for the inner loop $b = 1/2[0\bar{1}\bar{1}]$ and it is thus a perfect prismatic loop. By noting the apparent change in size of loops 1 and 2 when the sign of $(g \cdot b)s$ was changed (c.f. Figs. 1 and 3) the Burgers vector was uniquely identified as $1/2[\bar{1}\bar{1}0]$.

Table 1

$\bar{g}$	Loop 1	Loop 2	Loop 3
$\bar{1}1\bar{1}$	in	in	out
$\bar{2}02$	in	in	in
$0\bar{2}2$	in	in	out
$\bar{2}20$	in ($g \cdot b = 2$)	in ($g \cdot b = 2$)	in

Table 2

Prismatic				Glide		
$\frac{1}{2}[01\bar{1}]$	$\frac{1}{2}[\bar{1}0\bar{1}]$	$\frac{1}{2}[\bar{1}\bar{1}0]$	$1[010]$	$\frac{1}{2}[\bar{1}01]$	$\frac{1}{2}[0\bar{1}1]$	$\frac{1}{2}[\bar{1}\bar{1}0]$
0	1	0	1	0	1	1
1	0	1	0	2	1	1
0	1	1	2	1	2	1
1	1	0	2	1	1	2

From the results it is concluded that a single inclusion in Al-Si can generate both types of dislocation source to relieve stress. The particular mode which operates probably depends on the particle size and shape. Finally, it is noteworthy that many other glide dislocation segments with the same b were observed near the two outer loops. This suggests that small inclusions may be an important source of dislocations in metals.

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7. RESEARCH PLANS FOR CALENDAR YEAR 1977

Gareth Thomas

a. Microstructure, Properties and Alloy Design

Structural Steels. This continuing fundamental program is for investigating the effects of microstructure especially transformation morphology and retained austenite in quenched and quenched and tempered experimental vacuum melted steels. The objectives are to achieve desirable combinations of properties (strength, toughness) economically and without mechanical processing. Practical applications are for high strength, tough steels, e.g., in the mining and transportation industries. The steels are based on Fe/Cr/C.

Duplex Low Carbon Steels. New Fe/Si/C alloys have been designed to produce duplex ferrite-martensite structures by control of composition and heat treatment in the two phase ($\alpha + \gamma$) region followed by quenching. Fundamental studies are continuing to optimize morphological factors, volume fraction of martensite by examining the applicability of the "law of mixtures" developed for composites.

Magnetic Alloys

The principles of spinodal transformations are being applied to a new class of alloys based on Fe-Cr-Co so as to provide good combinations of strength, ductility and magnetic properties.

b. Ceramic Alloy Program

The objectives of this program are to obtain a better understanding of defects, phase transitions and relations to properties (physical in the case of the ferrite program, mechanical in the case of refractory carbides and nitrides) by precise applications of electron microscopy. Much basic information is needed as in this regard ceramic systems have been less well studied than metallic systems. We believe such research leads to the possibility of advances in design of ceramic microstructures for improved properties and technical applications.

c. High Resolution, High Voltage Electron Microscopy

Although we are obtaining considerably more information from lattice images than from conventional micrographs there are still a number of problems preventing us from attaining our goal of atomic resolution and identification. The resolution of conventional 100 kV instruments is limited. The thickness of specimens for image interpretation in terms of projected charge density must be less than 100Å, which is generally not possible for many materials. Both these factors can be overcome by utilizing higher voltage, high resolution instruments. Voltage increase also improves the possibility of studying beam-sensitive materials such as polymers and biological specimens. The interpretation of high resolution images, particularly for the

imperfect lattices which are often encountered in practical materials, requires more sophisticated theories than currently used. Image formation is still not experimentally routine and the output of lattice images is low when compared to conventional images. Again this situation should improve with better instrumentation. Specimen stages for in situ experiments (e.g., heating, cooling, environmental) are far below even lattice fringe resolution. It is to be expected that much more reliable conclusions can be drawn about materials behavior by actually observing reactions at the atomic level as they occur.

d. Point Defect Clusters and New HVEM Projects

1. Point Defect Clusters (K. H. Westmacott)

The object of this research is to understand in detail the nature of point defect clusters and the factors that affect the formation of various types of secondary defect. This knowledge is important for understanding the formation of defect clusters, particularly voids, in a reactor environment. Future research will apply the principles established from quenching studies to the more complex problems of radiation damage.

2. HVEM Equipment Plans (K. H. Westmacott)

650 kV Plans. We plan to modify the 650 kV microscope to adopt a side-entry specimen stage in an environmental chamber for new research programs. A grant of \$32K has been received from NSF to partially fund this project.

Plans for 1.5 MeV Microscope. Future programs involve the planning and management of the new microscope (installation expected 1978/79), see following article.

3. Future Programs

Proposed Organization of the 1.5 MeV HVEM Facility at LBL

Preliminary consideration has been given to how best to organize the LBL HVEM facility for optimum operation. Three separate but related interests may be identified: the need to ensure (1) full and efficient use of the electron microscope; (2) a mechanism for equitable sharing of the resource between the groups and users in various scientific disciplines within LBL as spelled out in the initial proposal; and (3) access is provided to other ERDA laboratory users, and that program duplication is avoided.

To meet all of these goals the following organization is being considered.

A local committee consisting of the principal investigators and the Facility Manager would draw up guidelines and general policies for implementation by the manager in the day to day running of the Facility. This committee would meet as often as necessary to fulfill this primary goal.

To assist in the establishment of general and longer term policies, and to make recommendations for implementing equitable time-sharing for existing and potential users both from inside and outside the ERDA community, an Advisory Board will be assembled. The Board should consist of between five and six members and it is proposed that respected scientists in the electron microscope community from industry, government, and universities be invited to participate. The Board should elect a small sub-committee for the purpose of reviewing and evaluating proposals from potential users and if necessary recommending priorities and time allocations on the microscope. It is envisaged that the Advisory Board would convene twice a year.

Finally, the third need could be met if representatives from all of the ERDA-supported HVEM facilities formed a coordinating committee to be convened annually at each location in turn.

Operational Procedures. By using shift principle (with two permanent microscopy operator-technicians available), the microscope should be operational easily to an average of 40 to 50 hours per week (based on past experience at Berkeley and elsewhere). The maximum number of users depends on the programs but we could envisage a total of about 50 per year.

The way the microscope should be utilized is by program. That is it should be set up for certain periods in order to accomplish specific tasks, e.g., set-up for in situ environmental projects, high resolution on beam sensitive specimens, biological programs and so on. This avoids constant shut down and change-over procedures. Time should be allocated in blocks sufficient to accomplish the particular project(s).

8. 1976 PUBLICATIONS AND REPORTS

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d. Powder Metallurgy

Milton R. Pickus, Principal Investigator

Introduction. Our research activities in powder metallurgy are based on the application of fundamental principles of materials science and high temperature chemistry to the design of new materials required in advanced technologies, and to the development of special processing techniques for obtaining them in useful forms. The characterization of these materials with respect to their mechanical, physical, and chemical properties is an important part of our effort. We are presently engaged in studying multiphase composites of intermetallic compounds in metallic matrices for application in severe environments, and rare-earth containing intermetallic compounds with useful magnetic properties. Thus, the common denominator of our current projects is the use of intermetallic compounds. These compounds, though long known to have interesting properties, have received little attention in the design of engineering materials, largely as a result of their intrinsic brittleness. The methods of powder metallurgy are particularly suited for incorporating these brittle compounds in non-brittle composites with unusual properties often otherwise unattainable.

1. SINTERING STUDIES OF RARE EARTH--IRON LAVES PHASE MAGNETOSTRICTIVE COMPOUNDS

M. Malekzadeh, M. P. Dariel and M. R. Pickus

The objective of this study was to examine the possibility of employing powder metallurgical processing techniques for the fabrication of high density Laves phase compounds in desirable shapes and sizes. These compounds exhibit magnetostrictions some two orders of magnitude greater than those of the currently used nickel and nickel alloys. Initially, samples were prepared by solid-state sintering. They exhibit very poor sinterability and had densities no higher than 82% of theoretical. A typical microstructure is shown in Fig. 1. The low densities have an adverse effect on both the mechanical and magnetic properties of the sintered compacts.

High densities were successfully achieved by employing a liquid phase sintering approach. Samples were prepared by blending two pre-alloyed powders with compositions on either side of the desired stoichiometry: 55 and 67 at%Fe, the balance, a mixture of terbium and dysprosium. The proportions used were calculated to yield as a final product the pseudo-ternary Laves compound, $\text{Dy}_{0.7}\text{Tb}_{0.3}\text{Fe}_2$. The iron-poor powder provided the liquid phase during sintering. This liquid reacted peritectically with the iron-rich component to form the desired Laves phase. Using this liquid phase sintering procedure, samples with 97% of the theoretical density were prepared (Fig. 2).

Fig. 1. Low density compacts prepared by solid state sintering. Black areas are mainly pores. (XBB 7511-8759A)

Fig. 2. Scanning electron micrograph of liquid phase sintered sample. Pores appear as black and oxides as white areas. (XBB 768-6887)

The static magnetostrictive behavior of the sintered compacts was determined using a conventional strain gage technique. The results obtained thus far (Fig. 3) indicate that both with regard to the magnetostrains attained, and the rate of approach to saturation, liquid phase sintering of these materials appears to be highly promising.

Fig. 3. Room temperature magnetostriction of liquid phase sintered $\text{Dy}_{0.7}\text{Tb}_{0.3}\text{Fe}_2$. (XBL 768-7302)

2. STRUCTURAL AND MAGNETIC STUDY OF SOME OXYGEN STABILIZED RARE EARTH--IRON INTERMETALLIC COMPOUNDS

M. P. Dariel and M. R. Pickus

A new series of oxygen stabilized intermetallic compounds was discovered in the course of our studies of sintered, prealloyed rare-earth iron powder samples. The composition of these compounds was determined and found to correspond with the formula $\text{R}_{12}\text{Fe}_{32}\text{O}_2$. The crystal structure conforms with space group $\text{Im}\bar{3}\text{m}$. Their presence has been observed in several R-Fe-O systems, with R = Gd, Tb, Dy, Ho, Er and Y. Magnetic measurements indicate that $\text{Y}_{12}\text{Fe}_{32}\text{O}_2$ is ferro-magnetic, while the compounds with R = Dy and Ho are ferrimagnetic. The magnetic ordering temperatures of these three compounds range from 180 K to 265 K. The data are summarized in Table 1.

Table 1. Magnetic data for some $\text{R}_{12}\text{Fe}_{32}\text{O}_2$ compounds.

Compounds	$\sigma^*(\mu_B/\text{g})$	$\sigma^*(\mu_B/\text{Unit Formula})$	T_c (K)
R = Y	62.7	32.4	183
R = Dy	89.4	61.9	262
R = Ho	90.3	61.4	222

* Saturation magnetization at 4.2 K (by extrapolation)

3. FRICTION AND WEAR OF DISPERSED INTERMETALLIC COMPOUNDS IN FERROUS MATRICES

Robert A. Riddle, J. Ling-Fai Wang and Milton R. Pickus

Materials with high wear resistance and low-frictional coefficients are of critical importance in the development of new energy systems. In a broader sense the availability of such materials would provide a basic way in which both energy and raw materials can be conserved by prolonging the lifetime of manufactured components. During the past year, our work was concentrated in two areas. Studies were made of the various theories of wear mechanism in order to evolve a coherent strategy for alloy design. Tests on a variety of materials were carried out to evaluate the performance and reliability of our friction and wear measuring equipment. It was found that design modifications and refinements were necessary and therefore part of our effort was diverted toward accomplishing these improvements. The proposed apparatus, which employs the pin on disk configuration, is shown schematically in Fig. 1.

Fig. 1. Schematic illustration of friction and wear apparatus. (XBL 7612-4504)

It was concluded from our study of wear mechanisms that dispersed intermetallic compounds would provide a materials system with highly desired properties, especially in situations where large contact pressures and inadequate lubrication are encountered. As compared with the carbides of tungsten and titanium, the intermediate hardness of the intermetallic compounds should be advantageous in providing resistance to abrasive wear. Additionally, the tendency of the intermetallic compounds to form diffusion layers with appropriate matrices should be effective in reducing fatigue and fracture modes of wear.

The composite samples used to test the apparatus and provide necessary background data were successfully prepared by powder metallurgy techniques. They consisted of a dispersion of the hexagonal Laves phase of the cobalt-molybdenum-silicon system in several matrices, including iron and stainless steels of different types. For comparison purposes samples consisting

only of the matrix material were prepared under similar conditions. In all cases, additions of the intermetallic compound markedly decreased the measured wear rate. A typical composite is shown in Fig. 2.

Fig. 2. Microstructure of a sintered composite of Co-Mo-Si Laves phase dispersed in an S16 stainless steel matrix. (XBB 760-10823)

4. RESEARCH PLANS FOR CALENDAR YEAR 1977

Milton R. Pickus

The success achieved in applying powder metallurgy techniques to the preparation of magnetostrictive rare earth--iron Laves phases opens new areas that will be investigated. There is evidence that these compounds have an axis of easy magnetization along the [111] direction. An effort will be made to take advantage of this by compacting the powdered compound in a magnetic field. It will be determined whether the anticipated alignment of the powder particles has the effect of lowering the magnetic field required for saturation. A lower saturation field should reduce the bias field required for optimum performance. Also, since some residual porosity must be anticipated, static magnetostriction measurements will be made on samples containing varying amounts of porosity. Such measurements will provide quantitative information concerning the effect of porosity on magnetostriction. For a more complete evaluation of these materials,

these tests will be supplemented by dynamic magnetostriction measurements in terms of applied bias field and frequency, as well as porosity.

In support of the superconductivity program, we will be developing a powder extrusion process that will provide long lengths of tape or wire with a range of porosities appropriate for infiltration. Long lengths will permit the winding of coils for use in superconductor performance evaluations.

Preliminary experiments with our rotating electrode powder making apparatus, while giving encouraging results, indicated a need for modifications. The equipment, which is now ready for further tests, provides for a rapid quench from the liquid state. We plan to investigate its potential for producing powders with metastable compositions. Such materials are expected to exhibit unusual mechanical and electrical properties.

In regard to another of our programs, it should be noted that although wear and friction have always been a source of technological problems, there has been virtually no effort in fundamental alloy design specifically oriented to address this challenge. Our plan is to develop a materials system consisting of compounds, covering a range of hardness, stability and crystal types, dispersed in matrices that provide adequate support and bonding. Such a system would have the inherent flexibility of providing materials whose properties can be tailored to fit a variety of technological requirements. Our past work has provided the basis for a versatile matrix. Studies will be made of the friction and wear characteristics of this matrix alone and with varying volume fractions of the dispersed compounds.

5. 1976 PUBLICATIONS AND REPORTS

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2. MECHANICAL PROPERTIES

a. Theoretical Problems in Alloy Design

J. W. Morris, Jr., Principal Investigator

Introduction. The research to be reported here can be conveniently divided into two parts. The first part includes our theoretical research activities in fundamental metallurgy. During the past year this research has concentrated especially on the nature of nature of microstructure and on the manner in which microstructural variables can be quantified and incorporated directly into the constitutive equations which determine material properties. The problem is being attacked from three different perspectives. The first, described under articles Nos. 1 and 2 following, includes an attempt to directly characterize the microstructures that might arise from simple nucleation and growth transformations in prototypic simple solids. Both theoretical and computer simulation techniques are used. The specific projects are: (1) atomistic simulation of the early stages of precipitation and coarsening in an Ising lattice, and (2) geometric study of idealized polygranular microstructures in a search for useful quantitative parametrizations.

The second approach, reported under article No. 3 following, has as its objective the direct determination of the structure-property relation for an idealized single crystal. The crystal is taken to be an ideal body containing a distribution of dislocations that may glide under an applied stress, and also containing a distribution of microstructural features that may act as barriers to dislocation glide, and which have prespecified properties. Using computer simulation and theoretical techniques, we then attempt to predict the mechanical equation of state of this crystal, hence predicting the rate of plastic deformation as a function of the temperature, the applied stress, and the nature and properties of the microstructural barriers. The result of the investigation is a precise specification of the mechanical equation of state of a simple prototype crystal.

The third approach is the study of the macroscopic constitutive relations which govern the plastic behavior of engineering materials. The portion of this work reported in article no. 4 following addressed the low stress creep behavior of superplastic materials, where both the proper form of governing constitutive equation and the role of the microstructure are controversial.

The second major part of our research is concerned with the actual design of new engineering alloys to meet advanced requirements in the energy area. During the past year our research has included three specific alloy design projects together with supporting basic studies. The first of these, reported in article no. 5

following, is a continuation of our research toward tough ferritic alloys for use at liquid helium temperature, the temperature encountered in a superconducting magnet and in other advanced cryogenic systems. Our previous research has demonstrated that ferritic Fe-Ni alloys can be processed to have an excellent combination of strength and toughness in liquid helium. Our current effort is directed toward better understanding of the role of microstructural features in establishing low temperature toughness.

While this research has lead to a series of alloys that exhibit outstanding toughness in liquid helium, the alloys all contain high concentrations of nickel, and, would, as a consequence, be expensive in commercial practice. For this reason we have inaugurated a second alloy design project that has as its objective the development of nickel-free cryogenic alloys for use at temperatures such as the temperature of liquefied natural gas at which large tonnages of cryogenic material are expected to be needed in the next few years. Our specific research is concentrated on the development of ferritic Fe-Mn alloys for cryogenic use, and is reported in article no. 6 following.

The third project, below, is a joint alloy design effort with Professor Gareth Thomas, and addresses the problem of designing very high strength, very high toughness austenitic alloys for use in retaining rings in large electrical generators. Given the engineering constraints in this application the alloy must be thermally processed using techniques which are applicable to thick sections. Our progress to date is reported in article no. 7 following.

1. THEORETICAL STUDY OF TWO-PHASE DECOMPOSITION AND COARSENING

E. S. Pundarika, K. Hanson, and J. W. Morris, Jr.

A variety of important metallurgical phenomena are controlled by the nature and kinetics of precipitation reactions and precipitate-coarsening processes. The relevant phenomena include precipitation hardening and aging processes in alloys and void formation and swelling in irradiated materials. The most striking influence on properties is often seen during the first stages of precipitation when the precipitates contain only a few atoms or unit cells and the precipitate distribution is far from equilibrium. While classical continuum theories of precipitation and coarsening give useful insight into the

initial stages of precipitation reactions a thorough understanding can only be achieved through theoretical study at the atomic level.

During the past few years several investigators have used Monte Carlo methods to study precipitation and coarsening reactions in the simplest realistic case: the binary Ising lattice in which atoms of two types (A and B) are distributed over the available lattice sites and are assumed to interact only with those atoms on immediately adjacent sites. If the relative energy of the A-B interaction is such that atoms have an energetic preference for neighbors of like kind then the clustering of A and B atoms will be thermodynamically preferred at low temperature. If the lattice is randomized by equilibrating it at high temperature where the configurational entropy is dominant, and is then "quenched" to some low temperature at which clustering is preferred a precipitation reaction will occur. In computer simulation the precipitation reaction may be followed in real time by assigning diffusional jump frequencies for the various types of atom exchanges which may occur, adjusting these to account for their relative effect on the energy of the whole system and using statistical techniques to select a statistical sequence of atom exchanges and waiting times.

While previous simulation studies of this type have yielded a number of interesting results the computer codes employed have been time-consuming and expensive to operate, with these undesirable consequences: (a) very few simulations have been published, none of which has been carried out to the times needed to clarify precipitate coarsening mechanisms; (b) the published simulations treat rather small lattices, and hence risk misleading results due to boundary effects; (c) the simulation procedures are such that an extension to more realistic cases, involving for example second or third nearest neighbor interactions, would involve very large computing costs.

Given the evident potential value of simulation studies of this type and the research background summarized above we began research with the initial objective of writing a computer code which would permit the efficient dynamic simula-

tion of precipitation and coarsening processes in large atom arrays. The code has been constructed. It is capable of treating two- or three-dimensional lattices of large size and arbitrary crystal structures, and appears to be more than an order of magnitude faster than previous codes. The increase in efficiency was obtained by modifying the procedure for selecting a statistical sequence of atom exchanges so that all redundant and irrelevant exchanges are ignored, and by optimizing the handling and updating of data in the computer. The code was verified by duplicating published results.

The code is being used principally to study coarsening processes in the early stages of precipitation. Some initial results are illustrated in Figs. 1 and 2. The results

Fig. 2. The evolution of energy with time for a two-dimensional square lattice of 6400 atoms, 20% B, at a reduced temperature $T/T_c = 0.58$. (XBL 7611-9954)

Fig. 1. The evolution with time of a planar square lattice of 6400 atoms, 50% B, at a reduced temperature $T/T_c = 0.58$. The dominant coarsening mechanism is the coagulation of adjacent clusters over this time period. (XBL 7611-9955)

obtained to date demonstrate that coarsening in this system occurs through simultaneous action of the Lifshitz-Slosov mechanism (atom evaporation and redeposition) and the Smoluchowski mechanism (direct coagulation of clusters). The coagulation mechanism dominates at early times but becomes less important as clusters grow and spheroidize. The rather complicated evolution of energy with time can be interpreted in terms of these mechanistic changes.

2. THE CHARACTERIZATION OF POLYGRANULAR MICROSTRUCTURES

The central problem in Physical Metallurgy (perhaps the central problem) concerns the manner in which the properties of a material are determined by its microstructure. If this general problem is solvable, its solution can best be phrased as a set of constitutive equations which functionally relate the physical properties to composition, thermodynamic intensities such as temperature and applied stress, and a set of constitutive variables which are sufficient to specify the relevant aspects of the state of the microstructure. Excepting semiquantitative expressions of the Hall-Petch type, which extrapolate the relation between mechanical properties and the mean grain size or mean dislocation density with some success, very little progress has been made in constructing useful constitutive equations for structure-sensitive properties. A major barrier to theoretical progress is the complexity and infinite variety of the microstructures which may be encountered in real materials and the resulting difficulty of identifying meaningful parametrizations which would allow the microstructure to be characterized by a manageable set of constitutive variables.

Given the complexity of the microstructure of real materials it is not at all obvious that a useful parametrization exists. If one does exist its simplicity will almost certainly have one of the following sources: (1) The mechanisms determining the value of the structure-sensitive property are relatively insensitive to microstructural details, and depend strongly only on characteristics such as the mean, moment, or extrema of the distribution of some dominant microstructural feature. (2) The physical processes establishing the microstructure are such that the microstructures of real materials are not arbitrary, but may be divided into geometrically distinct classes such that the members of each class are simply related in their essential geometric details. The first of these interpretations is assumed (almost always implicitly) in most theoretical discussions of the influence of microstructure on mechanical properties. The second often enters in a qualitative way in the discussion of experimental results on structure-property relations. While there are experimental indications that this second approach may be fruitful its promise is difficult to assess because of the experimental difficulty of measuring and tabulating geometrical data and the absence of a clear theoretical

framework to guide the geometrical comparison of different microstructures.

Given this background a research project was initiated to study the geometry of microstructure, with an initial emphasis on the polygranular microstructures generated by simple nucleation and growth processes. Computer simulation studies have been emphasized since this technique permits a precise specification of nucleation and growth kinetics and a rapid determination of geometric features of the resulting microstructures. Research progress during the past year is summarized under four task headings:

a. Microstructure Types

John E. Sanchez and J. W. Morris, Jr.

In this project we are investigating the various types of microstructure which may result from a simple prototype nucleation and growth process with the objective of providing a geometric classification. We assume an initially homogeneous polygranular body which transforms by a nucleation and growth mechanism to yield a homogeneous product. Nuclei of the new phase are presumed to form either homogeneously in the bulk of the original phase or heterogeneously on one of the preferred sites (grain boundaries, edges, or corners) that exist in the initial phase. The nucleation rate is assumed constant for each type of site but changes with the catalytic potency of the site and with thermodynamic conditions according to relations given by classical nucleation theory. After nucleation the grains are assumed to grow at a constant, isotropic rate until they impinge on one another.

The dependence of the nucleation rate on thermodynamic variables is such that the transformation will usually be dominated by nuclei which form on a particular type of site. The resulting microstructure will then depend on whether the dominant nucleation sites are "saturated" in the sense that they are consumed by nuclei before the transformation is completed. An analysis of the possible resulting microstructures then leads to the identification of the four geometric classes listed in Table 1.

An unsaturated transformation yields the characteristic Johnson-Mehl microstructure irrespective of the dominant nucleation site. Johnson-Mehl microstructures are geometrically identical. They differ only through a magnification factor which is expressed by the characteristic length $d_i^* = (N_i/G)^{-1/4}$, where N_i is the nucleation rate at the dominant site (i) and G is the growth rate. The microstructures resulting from saturated transformations depend on type of the dominant nucleation site and on the nature of the pre-existing microstructure. If the dominant site is the grain boundary the resulting microstructure will consist of rod-like grains which result from a two-dimensional Johnson-Mehl transformation of the boundary followed by perpendicular growth to impingement. They are hence characterized by two lengths: The scaling length (d_b^*) of the boundary JM process and the diameter (d) of the pre-existing

Table 1. Characteristic microstructures.

		Transformation Mode	
		Unsaturated	Saturated
Dominant Site	H -	JM	--
	B -	JM	BS
	E -	JM	BS
	C -	JM	CS (cellular)
JM: Johnson-Mehl Microstructure			
BS: Boundary Saturated Microstructure			
ES: Edge Saturated Microstructure			
CS: Corner Saturated Microstructure			

microstructure. If the dominant site is the grain edge the microstructure consists of platelets whose thicknesses scale with the characteristic length (d_E^*) of the one-dimensional JM transformation of the edge and whose lateral extension will scale with the prior grain diameter (d). If the dominant site is the grain corner the product microstructure is a "cellular" microstructure, consisting of three-dimensional cells with planar faces whose sizes will scale with the prior grain size (d). The resulting microstructure is the so-called "cellular" microstructure which has been the subject of some theoretical study by statisticians.

A simple criterion determines the type of the product microstructure in most cases. If site (i) of dimension (i) is the dominant nucleation site, then $t_i^* = (\dot{N}_i G)^{-1/4}$ is a characteristic time for completion of an unsaturated transformation through nucleation on this site, and

$$\tau_i = (\dot{N}_i d^{e-i} G^i)^{-1/1+i}$$

is a characteristic time for saturation of this site. If $\tau_i < t_i^*$ an i-saturated microstructure will usually be obtained; if $\tau_i > t_i^*$ the JM microstructure is anticipated. A more detailed analysis leads to results such as those in Fig. 1, where the geometric type of the product microstructure is plotted as a function of the thermodynamic conditions of the transformation.

The results of this research show that the microstructures typically resulting from simple nucleation and growth processes can be grouped into geometric classes and parametrized by one or a small set of variables. While restrictive assumptions have been made in this analysis, they appear to be at least approximately satisfied in a number of real transformations including the decomposition of austenite to pearlite in steel, the recrystallization reaction in several alloys, and ordering reactions in ceramics.

Fig. 1. The geometric type of the product microstructure resulting from a simple nucleation and growth transformation from a high-temperature to a low-temperature phase. T_0 is the equilibrium temperature between the two phases, σ_g is the grain boundary tension of the initial phase, and σ is the interfacial tension between the two phases. The initial grain size is taken to be 5×10^{-3} cm. (XBL 771-4922)

b. Computer Simulation of Microstructure

K. W. Mahin, K. Hanson and J. W. Morris, Jr.

Further studies of some of the theoretically interesting microstructures discussed above have been carried out through the development of a computer simulation program. Two transformation classes have been fully characterized by this method: (1) saturated nucleation and growth from random sites: cellular microstructure and (2) homogeneous nucleation and growth: Johnson-Mehl microstructure. Variations on these basic types, such as the growth of elliptical or odd-shaped particles and specification of viable nucleation sites, are also possible. An example of this is the nucleation of particles on a BCC lattice under time and growth conditions similar to the cellular and Johnson-Mehl microstructure types.

The computer simulation has been designed to allow a three-fold characterization of a given microstructure type. A typical microstructure is first generated in three dimensions from theoretically defined nucleation and growth functions enabling identification of all nucleation sites and times as well as the various growth rates. From this information computer drawn serial sections of the microstructures can be generated to afford optical analysis of the shape. More precise shape studies are performed by utilizing statistical methods to obtain frequency distributions of various geometric parameters as shown in Figs. 2 and 3. More detailed

Fig. 2. Comparative distributions of geometrical features in planar sections of the Johnson-Mehl and cellular microstructures: (a) grain areas; (b) intercept lengths along a randomly oriented line. (XBL 7612-7967A)

explanations of code design and simulation procedures are available in Refs. 1 and 2.

In order to be able to precisely distinguish between the products of the transformation classes, it has been necessary to establish which of the various geometric features of the microstructure was the most shape sensitive. To determine this, various histograms have been plotted for both the Johnson-Mehl and cellular microstructure types. Figures 2(a) is an overlay of the $A/\langle A \rangle$ plots for the two microstructure types. In this case the distributions are distinctly different. However, when the standard parallel line grid method for isotropic materials is used to obtain intercept length distributions for both microstructure types, it is found that

the shape sensitivity of this parameter is minimal, Fig. 2(b). Other geometric parameters show varying degrees of sensitivity. The grain cross section diameter obtained from the square root of the area follows the area parameter in degree of shape sensitivity. Since it has been established² that these shapes are unique to the particular microstructure type, it is apparent that a plot of the areas of the grain cross sections is necessary in order to accurately determine the dominant transformation process.

Although the computer generated results can only be directly compared with the theoretical predictions for the corresponding transformation class, it is interesting to compare the correlation of the results for the ideal microstructure to those obtained for real microstructures. Figure 3 shows an overlay of the plots of grain

Fig. 3. Comparative distributions of grain diameter ($D = A^{1/2}$) in the Johnson-Mehl microstructure (solid line) and in recrystallized Armco iron (dotted line: Scheil and Wurst).³ (XBL 766-7007)

section diameters for a real microstructure (Armco iron obtained by Scheil and Wurst)³ designated by the dotted line and the ideal Johnson-Mehl microstructure shown by the solid line plot. Other similar comparisons have shown that the idealizations necessary for the transformations studied do not cause the data to deviate too much from reality. Hence characterizations of these types can be used to study further transformation types and may provide a basis for classification of real microstructures according to dominant transformation mechanisms.

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2. K. W. Mahin, M.S. thesis, LBL-5125.
3. Scheil and Wurst, Ztsch. Metallkunde 28, 340 (1936).

c. Interactive Analysis of Microstructures

D. Gutzler, K. W. Mahin, and K. Hanson

A peripheral code was written which extended the capabilities of the simulation program to analysis of serial sections of real microstructures. The code utilizes the VISTA 250 interactive display system at the LBL Computer Center. A human operator copies points from a transparency of a microstructure onto the VISTA screen with a light pen. The code connects the input points with straight lines. The fully constructed microstructure is then fed into the main program for analysis. Thus cellular microstructures may be precisely defined simply by inputting the grain intersections. Microstructures of this type have been tested, establishing the accuracy of this approach to microstructure analysis. This method could be extended to microstructures with curved grain boundaries by approximating each boundary as a series of connected line segments.

d. Three-dimensional Characterization of the Cellular Microstructure

K. Hanson

While many of the interesting geometric properties of a microstructure emerge from an analysis of planar sections, others can only be obtained from a full three-dimensional characterization. Examples include the distributions of volumes, surface areas, edge lengths, and numbers of contacting neighbors, the distribution of diffusion path lengths through grain surfaces or along edges (which is of considerable interest in the analysis of atmospheric contamination and in certain radiation damage problems), and the connectivity of phases in polyphase microstructures. Three-dimensional analysis can be carried out with the code described in preceding article No. 2b, using "serial section" techniques of the sort employed in the experimental study of real microstructures. However, since many sections must be analyzed to obtain reasonably complete three-dimensional data, this approach is expensive in computing time.

If we restrict attention to microstructures of the "cellular" type, that is, microstructures obtained through isotropic growth from a distribution of nuclei which form simultaneously, it is possible to construct an efficient code which will completely analyze the microstructure in three dimensions. The code is based on the geometric simplicity of cellular microstructures. Such a microstructure is completely described by a list of the nucleation sites. Grain corners are then points which are equidistant from four adjacent nucleation sites which are the nearest sites to the corner point. Grain edges are straight lines which connect corners, and contain points which are equidistant from the three nearest nucleation sites. Grain surfaces are planes, equidistant from two nucleation sites, which are bounded by corners. For the purposes of computer analysis the cellular microstructure is best represented by a stored graph in which nodes

represent grain corners in the microstructure and each node is connected to four other nodes by paths representing grain edges. All interesting three-dimensional geometric information can be extracted from this graph.

We have constructed an efficient computer code for creating and storing the connected graph

NUMBER OF FACES / GRAIN

Fig. 4. The distribution of the number of faces per grain in a cellular microstructure obtained by isotropic growth from randomly distributed nucleation sites. (XBL 773-591)

EDGE LENGTH

Fig. 5. The distribution of cell edge lengths within a cellular microstructure. (XBL 733-592)

described. Efficient searching and storing algorithms enable our code to create a connected graph for a periodic cube possessing one hundred nucleation sites using only seven seconds of CDC 7600 computer time. Figures 4 and 5 show the distribution functions for the number of faces (i.e., number of neighbors) per cell and the edge length, respectively, for a cellular microstructure containing 300 nucleation sites. Distributions for cell volumes and surface areas can also be calculated. Furthermore, linear programming techniques can be used to find the shortest edge path through the resulting cellular microstructure. Thus, the simulation of a three-dimensional cellular microstructure should enable study of a variety of interesting problems.

3. PLASTIC DEFORMATION OF IDEALIZED CRYSTALS

The plastic deformation of a crystal is accomplished through the motion of dislocations. The dislocation motion is impelled by the applied shear stress and opposed by the inherent resistance of the crystal lattice (the Peierls-Nabarro barrier) and by microstructural features including point defects, precipitates, and other dislocations which function as pinning points and barriers to dislocation glide.

For some time we have been engaged in a combined computer simulation and theoretical study of plastic deformation through dislocation glide in the idealized case in which the dislocations are modeled as flexible strings of constant tension and the microstructural obstacles to glide are treated as point barriers of given properties. The investigation concerns the variation of the critical resolved shear stress for athermal glide and the velocity of thermally-activated glide at finite temperature as functions of the configuration of gliding dislocations, the applied stress, and the nature and strength of the obstacles. Particular attention is paid to the statistical factors which control the velocity and characteristics of glide.

Research progress during the past year can be summarized under three headings.

a. The Influence of Array Size on Dislocation Glide through Randomly-Distributed Obstacles

S. Altintas, K. Hanson and J. W. Morris, Jr.

The initial problem studied in this research concerned the glide of a single dislocation through a field of randomly-distributed point obstacles of given properties. This research^{1,2} showed that both the critical resolved shear stress for athermal glide and the velocity of thermally activated glide at low temperature are essentially determined by the properties of statistically external configurations which are the most stable configurations of obstacles encountered by the dislocation as it sweeps through the array. In the limiting case in which the size of the array approaches infinity the

properties of these configurations can be accurately approximated by analytical techniques.^{3,4} Computer simulation studies have shown, however, that the properties of the most stable configurations are sensitive to the array size, and converge very slowly to their limiting values. This result has two significant consequences: (1) since the microstructural obstacle arrays of physical interest are finite, the variation of glide properties with array size should be taken into account in physical theories; (2) since the glide resistance of the array converges slowly with array size it is difficult to check the precision of the analytic equations^{3,4} developed in earlier research.

During the past year we constructed a simple analytic technique for estimating the influence of the array size on glide properties. The approach follows from the addition of two assumptions to the theoretical development in Ref. 3: first, that an obstacle array of arbitrarily large size contains a high density of strong configurations, and second, that the strong configurations encountered in glide through a finite array are subsets of these. Using these assumptions a simple set of equations was derived to estimate array size effects. Results are exhibited in Figs. 1 and 2. Figure 1 shows the

Fig. 1. The critical resolved shear stress (τ^*) as a function of obstacle strength (β_c) for a square array of 10^6 randomly distributed points. (XBL 771-4911)

dimensionless critical resolved shear stress for athermal glide (τ^*) as a function of the dimensionless obstacle strength (β_c) for a square array of 10^6 points. Figure 2 shows the value

Fig. 2. The variation of the obstacle strength necessary to prevent athermal glide of a single dislocation under dimensionless stress $\tau^* = 0.001$ as a function of array size. (XBL 771-4912)

of the obstacle strength (β) required to prevent athermal glide under given applied stress as a function of the array size. In both cases the agreement between theory and computer experiment is good.

While further refinement of the analysis is needed to account for effects which intrude at higher obstacle strengths and for the influence of boundary conditions in arrays of small size, the results obtained during the past year suggest that we are close to a complete solution to the problem of single dislocation glide through point barriers.

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2. J. W. Morris, Jr. and D. H. Klahn, J. Appl. Phys. 45, 2027 (1974).
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b. Dislocation Glide through Arrays of Unlike Obstacles*

S. Altintas, K. Hanson and J. W. Morris, Jr.

In glide through a real crystal a dislocation contributing to plastic deformation will generally encounter microstructural barriers of more than one type. In the case of glide through a crystal

containing both forest dislocations and small precipitates or solute atoms, for example, both obstacle types will contribute to the pinning force on the dislocation. In earlier work¹ we derived analytic equations which accurately estimate the critical resolved shear stress for athermal glide, the velocity of thermally-activated glide at low temperature, and the properties of the strength-determining configurations for arbitrary obstacles properties, given that the obstacles may be treated as point barriers to glide.

During the past year we extended these results along two lines. First, we verified that the theory does give good estimates of such characteristics of the strength-determining configuration as the density of obstacle types along the dislocation (which differs from the average density within the array) and the mean segment length. The mean dislocation segment length in the strength-determining configuration is plotted in Fig. 3 as a function of the fraction

Fig. 3. (a) The mean dislocation segment length in the strength-determining configuration for glide through a mixed array of two obstacle types, plotted as a function of the fraction of relatively strong obstacles. (b) Data in the range of the fraction of strong obstacles (x_s) up to 10%. (XBL 771-4908, -4797)

of weak obstacles for glide through a mixture of two obstacle types. The data obtained through

Fig. 4. Critical resolved shear stress vs. fraction of strong obstacles in a mixture of two obstacle types. (a) Mixture of obstacles having strengths $\beta_s = 0.1$ and $\beta_w = 0.05$. (b) Mixture of obstacles having strengths $\beta_s = 0.1$ and $\beta_w = 0.01$. (XBL 771-4910, -4909)

computer simulation are in good agreement with the theory, and confirm the surprising prediction that the mean segment length passes through a maximum as the fraction of strong obstacles is increased.

Secondly, we investigated simple approximations to the theory. Previous researchers had speculated that the critical resolved shear stress for glide through a mixture of two distinct obstacle types might be expressible as either the linear mean or the quadratic mean of the critical stresses for the two obstacle types alone. We found that the theoretical solution for the critical resolved shear stress can be phrased as the sum of the quadratic mean of the stresses for the individual obstacles plus a correction term which is small unless there is a very large population of relatively weak obstacles. The simple expression

$$(\tau^*)^2 = \sum_{i=1}^n x_i (\tau_i^*)^2$$

provides an excellent estimate for the critical resolved shear stress (τ^*) for glide through an array having fractions x_i of obstacles of type (i), where τ_i^* is the stress for athermal glide through an array of obstacles of type (i) alone, as is illustrated for the case of two obstacles in Fig. 4. The estimate is less accurate when there is a strong preponderance of relatively weak obstacles. This case is being investigated further.

*Supported by the National Science Foundation through Grant # DMR75-08163.

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c. Simultaneous Glide of Interacting Dislocations*

K. Hanson and J. W. Morris, Jr.

The plastic deformation of real crystals is influenced by the interaction of the gliding dislocations with one another as well as by their interaction with microstructural obstacles. To study this factor we constructed a computer code which permits the simulation of the simultaneous glide of interacting dislocations of given type.

During the past year this code was utilized to study two prototype problems which are illustrated in Fig. 5: the glide of an initially periodic train of interacting dislocations through a random array of point obstacles of given properties, and the glide of a periodic vertical array of like dislocations (a simple tilt boundary), located in parallel glide planes each of which contains a random distribution of point obstacles. The critical resolved shear stress for athermal glide was found to depend on the following variables: (1) the dimensionless obstacle strength (β_c); (2) the mean spacing (h) between dislocations (in terms of the mean spacing (l_s) between obstacles in the plane); (3) the effective line tension (λ) of the dislocations.

The central result of this investigation was the observation, illustrated in Fig. 6, that all data taken (more than 300 cases) are well represented by the simple relation

$$\tau^* = \tau_0^* \exp(-\sqrt{Q})$$

where τ^* is the stress for athermal glide of the array of interacting dislocations, τ_0^* ($= 0.8871 \beta_c^{3/2}$) is the theoretical stress for athermal glide of a single dislocation, and $Q = T \beta_c^{-1/2}$, where $T = \pi^2/3\lambda h^2$ is the nondimensional gradient of the stress seen by a single dislocation on displacement from its equilibrium position in an infinite train of dislocations separated by distance h . The athermal glide stresses for both planar and vertical arrays are well fit by the equation. While the theoretical source of this relation has not yet been identified, its simplicity suggests that the theoretical treatment of plastic

(a) 5 Parallel glide planes

(b) 8 Dislocations in series

Fig. 5. Illustration of the glide of interacting dislocations in two cases: (a) the dislocations are stacked vertically in parallel glide planes (only the obstacles in the lowermost glide planes are shown); (b) the dislocations are in series within a single glide plane. (XBL 764-6679)

Fig. 6. The critical stress for athermal glide of interacting dislocations as a fraction of the critical stress (τ_0^*) for glide of a single dislocation, plotted as a function of the dimensionless parameter Q . (XBL 773-5194)

deformation through glide of interacting dislocations may not be as difficult as has previously been supposed.

A second interesting result of this study concerns the nature of glide in a vertical array of dislocations (low angle boundary). There are two possible glide mechanisms: the array may glide as an intact unit or it may dissociate to liberate dislocations onto the most favorable glide planes. We observed that when the maximum interaction stress between dislocations on adjacent glide planes is greater than 8% of the critical resolved shear stress the array remains intact during glide. If the maximum interaction is less than 3% of the critical stress the boundary dissociates. In intermediate cases the tendency to dissociate depends on the statistical fluctuation of strength between adjacent glide planes.

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4. LOW-STRESS BEHAVIOR OF SUPERPLASTIC MATERIALS

D. Grivas and J. W. Morris, Jr.

During the past year our research on the mechanical equation of state of real alloys was concentrated principally on the low-stress creep of materials which behave superplastically at higher stresses. The specific materials studied were the Pb-Sn eutectic and Al-Zn eutectoid alloys. The reason for our concentration on these materials was two-fold: (1) Superplastic materials are known to obey a rather simple mechanical equation of state. The mechanistic source of this equation of state and of the unique superplastic creep properties observed at intermediate stresses is of considerable fundamental interest. (2) There is a decided controversy over the behavior of superplastic materials at low stress. The equation of state may be written in the power law form

$$\dot{\gamma} = A\tau^n,$$

where $\dot{\gamma}$ is the steady-state shear strain rate, τ is the shear stress, n is the stress exponent, and A is a coefficient which includes the effects of temperature and grain size. At high stress $n = 4-7$, the activation energy is near that for bulk diffusion, and conventional creep is observed. At intermediate stress $n \sim 2$, the activation energy is near that for grain boundary diffusion, and the creep is superplastic. At low stress, however, investigators differ on the appropriate values of the activation energy and the stress exponent. Some results (on Al-Zn) give $n=1$ and an activation energy appropriate to grain boundary diffusion, suggesting a grain boundary creep mechanism of the Coble type. Other results, both on Al-Zn and Pb-Sn, give $n=3$

and an activation energy appropriate to bulk diffusion, suggesting a creep mechanism dominated by dislocation climb.

The reported observations of a Coble creep type of low stress deformation are confined to the Al-Zn eutectoid. We therefore conducted low-stress creep tests on superplastic samples of this alloy, using the apparatus and test techniques developed in this laboratory by Dorn and his co-workers. The results, exhibited in Fig. 1,

Fig. 1. The steady-state low-stress creep of Al-Zn eutectoid at high temperature, showing superplastic behavior (stress exponent $n=2$) at higher stress and a clear shift to a stress exponent $n=3$ at lower stress. (XBL 771-4918)

showed a consistent stress exponent of 3 at low stresses, in agreement with available data on other superplastic materials and with the results of several of the investigators who previously studied Al-Zn. No evidence for Coble creep was found, even though the results were extended to stresses well below those at which other investigators had claimed clear evidence for this mechanism.

Since merely adding data to one side of an experimental controversy rarely resolves it we began a detailed investigation into the nature of the low-stress creep behavior. During the past year the study concentrated on the mechanical characterization of low stress creep. For experimental simplicity the principal research material was the Pb-Sn eutectic alloy.

Some of the results of this study are shown in Fig. 2, which illustrates intriguing facets of the low-stress creep behavior. The value of the pre-factor (A) in the equation of state depends on the initial grain size of the sample crept under low stress, but is not changed by grain growth during testing so long as the stress is kept in the $n=3$ region. If, however, the sample is then tested at stresses in the $n=2$ region the samples show the behavior appropriate to its current grain size, and, if subsequently re-tested at low stress, will exhibit a new value of the pre-factor (A) which is also appropriate to the current grain size. These phenomena give rise to the curious hysteresis behavior shown by the data in Fig. 2.

Fig. 2. The steady-state low stress creep behavior of the Pb-Sn eutectic alloy, showing superplastic creep ($n=2$), the low stress creep mechanism ($n=3$) and hysteresis effects obtained in a cyclic sequence of creep tests. (XBL 771-4919)

The results shown in Fig. 2 are consistent with an hypothesized dislocation mechanism whose microstructural consequences are testable experimentally. The appropriate microstructural studies are in progress.

5. Fe-Ni CRYOGENIC STEELS

This research program was initiated four years ago with the objective of developing tough ferritic alloys for cryogenic use to 4 K. Its practical results to date include the development of new thermal processing techniques to control the microstructure and grain size of steels of

intermediate nickel content. These have been applied to a laboratory Fe-12Ni-0.25Ti alloy and to commercial "9Ni" steel to produce alloys having an excellent combination of strength and toughness to 4 K.

The microstructural devices used to achieve outstanding cryogenic toughness were two: (1) refining the microstructure to ultrafine grain size, and (2) incorporating a distribution of retained austenite into the refined matrix. A reasonable experimental control has been established for these microstructural features in the steels studied to date. However, the precise role played by grain refinement and by retained austenite in establishing the toughness of cryogenic steels remains unclear. Further progress in the development of new cryogenic alloys depends in an important way on the understanding and more efficient use of these microstructural features. Our current research is hence aimed toward a clearer understanding of the role of microstructure in determining the properties of cryogenic steels. During the past year three research tasks were undertaken:

a. Mechanisms of Microstructure Refinement During Thermal Cycling*

C. K. Syn and J. W. Morris, Jr.

In prior research¹⁻³ a thermal cycling technique was used to refine the grain size of 8 to 14 Ni alloys, imparting an excellent combination of strength and toughness to 4 K. The thermal cycling technique is essentially a repeated alternation of austenitization and austenite + ferrite two-phase decomposition with intermediate water or air cooling.

The exact mechanisms of microstructure refinement during thermal cycling are not yet clear. A TEM survey of the evolution of microstructure during thermal cycling was hence undertaken to specify the stages involved in grain refinement and to clarify why an alternate cycle (heating to γ and then heating to $\alpha + \gamma$ range of the phase diagram) seems essential to achieve ultrafine-grained microstructure. Initial results obtained with 9Ni steel are shown in Fig. 1.

Figure. 1. Microstructural evolution through the thermal cycling. The highly dislocated martensite laths of 1A structure after the first austenitization and subsequent water quench break into tempered martensite of cells and subgrains and austenite nucleated and grown along the lath boundaries during the first two-phase decomposition. The austenite transforms back to highly dislocated martensite as in 1B upon subsequent water quench. During the second austenitization (2A) and two-phase decomposition (2B) with subsequent water quench the structural transformation is repeated in finer scales. (XBB 769-8361)

The grain refinement appears to come from two principal sources: the nucleation and growth of austenite in martensite lath boundaries and the tempering of martensite during the ($\alpha + \gamma$) treatment. The austenites nucleate and grow along lath boundaries, then transform on quenching to highly dislocated martensites aligned rather parallel to the previous martensite lath boundaries. At the same time the original martensite undergoes extensive recovery due to cell wall and low angle grain boundary formation. This second process seems critical to microstructure refinement. The cell and low angle grain boundaries break up the martensite laths and establish a crystallographic misorientation between adjacent cells and grains. During subsequent transformation the misorientation seems to lead to the elimination of the "packet" alignment of adjacent laths by introducing martensites of different orientation.

This important process is under continuing investigation. Examination of microstructural change in time sequence during the two phase decomposition and subsequent steps is planned for the coming year.

*Supported by the Office of Naval Research under Contract N00014-75-C-0154.

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b. The Influence of Retained Austenite on the Properties of Fe-Ni Cryogenic Steels*

C. K. Syn, B. Fultz and J. W. Morris, Jr.

To determine the relation between microstructure and the effect of the retained austenite on the fracture toughness several series of Charpy specimens of 9Ni steel were given heat treatment and/or tempering such that each series had different grain size. Fracture toughness tests were performed using the three point bending method. The initial result of these tests was surprising. Regardless of the grain size, all the tempered specimens showed similar values of toughness (within ~10%) at 77 K while the untempered series showed drastically different values for different grain sizes. This result manifests the dramatic beneficial effect of the austenite introduced by tempering. However, a closer examination of the load-crack opening displacement (COD) diagrams revealed that the crack propagation is unstable when the microstructure is coarse. In earlier fracture toughness tests of fully microstructure-refined and unrefined 9Ni steels, the levels of the maximum load on fracture were rather similar at 77 K, but the crack propagation modes were different while at 4 K the maximum load levels and fracture modes were drastically different. It seems that the toughness at high temperature (>77 K) is controlled by the gettering effect, but as the temperature goes

down the mechanical stability of the retained austenite seems to control the fracture mode and toughness.

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c. The State of Order in Fe-Ni Martensite

S. Chen and J. W. Morris, Jr.

The iron rich martensitic Fe-Ni base alloys (Ni concentration <29%) show extra diffraction spots which closely resemble ordering superlattice diffraction spots in addition to matrix martensitic diffractions in electron diffraction patterns. The high resolution dark field micrographs also exhibit an ~10Å size ordered precipitate morphology. The Ni₃Fe long range order in Ni rich Ni-Fe alloys has been identified and well studied, as has NiFe long range order in Fe-Ni alloys with Ni concentration close to 50% has been found. Moreover, several researchers have reported the existence of Fe₃Ni ordering in ~25% Ni and ~31% Ni. Since the possible existence of the ~10Å ordered precipitates is important both to mechanical properties and to martensitic transformation mechanisms, we did additional research.

The similarity of the atomic diffraction factors of Fe and Ni atoms makes electron diffraction study difficult. Neutron diffraction has the advantage of revealing the magnetic diffraction factor which may help resolve the diffraction details of Fe-Ni superlattice structures which are hard to resolve by electron diffraction. An Fe-12Ni sample which had been heat treated at 550°C for 1 month was sent to the Oak Ridge National Laboratory for neutron diffraction study and the data clearly showed an extra {100} superlattice peak. Therefore Fe-6Ni, Fe-12Ni, Fe-25Ni, and Fe-31Ni were made and heat treated at 550°C for two weeks for neutron diffraction analysis. However, none of the samples listed above showed superlattice peaks. The previously observed {100} peak proved irreproducible, even on reexamination of the sample which had previously shown it. The ordered peak appears to have been an experimental artifact in the earlier studies.

On close examination, it was found that the extra diffraction spots in the Fe-Ni alloy pattern are not due to an ordered superlattice structure but to the passivating oxide layer which is known to be formed spontaneously on the surface of Fe-Ni alloys exposed to air at room temperature. A subsequent TEM study of this passivating oxide layer yielded interesting results relevant to the low temperature corrosion behavior of Fe-Ni martensite.¹

The collected experimental evidence argues that no ordered structure exists in Fe-Ni alloys. The previous research data are questionable. Recent independent neutron diffraction studies by Winchell and coworkers (private communication) support this conclusion. Recent Auger electron spectroscopy studies of the oxidation of Fe-Ni

alloys support our observation of oxide passivating layers.

1. S. Chen and J. W. Morris, Jr., LBL-4911, Met. Trans. A (in press).

6. Fe-Mn CRYOGENIC STEEL*

The increasing demand for inexpensive cryogenic materials has generated considerable research in the alloy design area. Two general research directions may be identified: (1) the reduction of nickel content in commercial Fe-Ni steels; (2) the development of new alloys whose composition is based on the replacement of nickel by cheaper alloying elements.

Fe-Ni steel seems to owe its excellent low temperature mechanical properties largely to the inherent toughening role of nickel in the iron lattice. Nickel reduction, therefore, has a certain limitation unless it is accompanied by a complicated modification of the composition and microstructure. Hence available low-nickel cryogenic alloys depend on compositional tuning together with relatively complex thermal treatment, and still contain 5% or more of the expensive Ni addition.

Our research for an alternative cryogenic steel has focused on the Fe-Mn system. From the economic point of view, Mn is one of the least expensive alloying agents in steel. Metallurgically Mn affects the solid-state phase transformation of steel in much the same way as Ni does. With a moderate concentration of Mn, Fe-Mn steel has a dislocated martensite structure (bcc) which ensures inherently good strength at low temperature. However, the steel must be suitably processed for cryogenic use.

In an effort to design a new cryogenic Fe-Mn steel we have been studying the effect of microstructural change and phase stability on the low-temperature mechanical properties. This research has taken two distinct paths. Low-Mn (bcc) alloys have excellent strength at low temperatures but poor toughness. Our research on these alloys has concentrated on the modification of microstructure to improve toughness. High-Mn (fcc) alloys have good low temperature toughness but low strength. Our research on these alloys has addressed the problem of finding suitable alloy additions for precipitation hardening.

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a. Influence of Austenite and ϵ -Martensite on the Properties of 12Mn Steel

S. K. Hwang and J. W. Morris, Jr.

In designing a cryogenic Fe-Mn steel it is essential to understand and utilize the influence

of the different phases which co-exist in the microstructure. We have specifically investigated the effects of retained γ (fcc) and ϵ (hcp) phases on the low temperature impact toughness of Fe-12Mn-0.2Ti.

The initial structure of the alloy principally consists of dislocated martensite (α' , bcc) with a small admixture of the ϵ phase, approximately 15 vol%. To introduce controlled distributions of the γ and ϵ phases the alloy was tempered in the two-phase ($\alpha + \gamma$) region, either directly or after a cold-work treatment.

Fig. 1. Fe-12Mn-0.2Ti. (a) Charpy impact energy at -196°C (CVN) and vol% of γ and ϵ after direct-tempering at different temperatures for 4 hours. (b) Same as (a) except the specimens were cold rolled 50% at room temperature. (c) Suppression of the ductile-to-brittle transition by each treatment. (XBL 762-6408B)

The Charpy impact energy at -196°C was measured for each different treatment and the results are plotted in Fig. 1(a) and (b) with corresponding phase analyses data. Fig. 1a is for the case of direct tempering while Fig. 1(b) is for cold worked and tempered specimens. These data support the conclusion that the retained γ phase has a significant influence on the cryogenic toughness whereas the ϵ phase has a negligible effect. In fact the peak-to-peak correspondence of the vol% γ and the fracture energy (denoted as CVN) in Fig. 1(b) is excellent. It should be noted that the rapid increase of ϵ phase is an indicative of decreasing γ stability thus deteriorating impact energy.

The cold working prior to the two phase tempering was found to be extremely useful for two reasons: (1) it enhances the $\alpha' \rightarrow \alpha + \gamma$ decomposition rate through increasing dislocation density and (2) it prevents directional growth of the reverted γ by transforming the preexisting ϵ phase to α' . The resulting structure consists of an ultrafine distribution of α' (equilibrium ferrite), and γ , with markedly improved toughness.

The suppression of the ductile-to-brittle transition temperature by the simple tempering and the cold work plus tempering treatments is shown in Fig. 1(c). In addition to the excellent impact toughness the latter treatment was shown to yield a considerably high yield stress (1179 MPa) and good K_{IC} value (100 $\text{MPa}\sqrt{\text{m}}$) at -196°C . The potential of the processed Fe-12Mn-0.2Ti alloy for cryogenic use is promising if a proper adjustment is made between the high yield stress and the slightly insufficient toughness.

b. 8Mn Cryogenic Steel

S. K. Hwang and J. W. Morris, Jr.

By deformation processing an Fe-12Mn-0.2Ti steel can be made strong and tough at cryogenic temperatures. However, for an alloy steel to be seriously considered for production it is always desirable to avoid room temperature deformation processes. We therefore conducted research to obtain a similar microstructure by thermal treatment alone.

We first attempted to reduce the grain size of the 12Mn steel by thermal cycling techniques. Unfortunately the initial result was not successful. The reason is the presence of ϵ phase in the as-quenched structure. By regenerating a sheet-like γ phase it interferes with the nucleation of refined γ when the alloy is treated in the two-phase ($\alpha + \gamma$) range.

Given this result we decided to apply the same technique to an ϵ -free martensitic structure. The composition chosen for this purpose was Fe-8Mn-0.2Ti. The sample was thermally cycled to the austenitic region and to the two-phase region successively, in a process very similar to that used for Fe-Ni steels.

The result was largely successful. The grain size was reduced from 70μ to $1\sim 5\mu$ after thermal

cycling with a concomitant substantial improvement in cryogenic mechanical properties as shown in Fig. 2. The as-quenched (denoted as A.S.)

Fig. 2. Fe-8Mn-0.2Ti. Improvement of the cryogenic mechanical properties by grain refining and retained austenite treatments. All processings are thermal treatments alone. (XBL 769-7594)

8Mn steel is extremely brittle; the ductile-to-brittle transition in Charpy test occurs at room temperature and there is almost negligible tensile ductility at -196°C . By grain refinement the transition was suppressed to below -100°C and a considerable increase of total elongation (T.E.) and reduction in area (R.A.) was obtained without any loss of yield stress (σ_y) or ultimate tensile stress (σ_{UTS}). The transition temperature was suppressed further by introducing some refined γ into the grain-refined structure. The net decrease of the transition temperature, therefore, is approximately 180°C .

From the study of Fe-8Mn-0.2Ti we conclude that a satisfactory grain size reduction, with significant improvement of cryogenic mechanical properties, can be achieved by thermal treatment alone if a suitable starting structure is chosen. It must be noted, however, that the 8Mn steel is too brittle in the as-quenched condition; $T_c = 25^{\circ}\text{C}$ compared to -50°C for 12Mn steel. If the same degree of the T_c suppression is obtained in modified 12Mn or slightly lower Mn composition the overall effect will be significant. This research is presently under way.

c. Precipitation-Strengthened Austenitic Fe-Mn Alloys

K. M. Chang and J. W. Morris, Jr.

The fundamental objective of this investigation was to achieve a uniform distribution of fine intermetallic precipitates in austenitic Fe-Mn alloys to provide improved strength. After a survey of possible precipitate species titanium

was chosen, and was added to about 2 wt% in completely austenitic Fe-28Mn and in ϵ -phase bearing Fe-20Mn alloys. The precipitation of the intermetallic compounds from the Fe-Mn-Ti solid solution was then studied. The precipitate was identified as the hexagonal Laves phase of Cl_{14} (MgZn_2) type, with chemical composition $\text{Fe}_2(\text{Ti,Mn})$. No transition phase was observed in the aging temperature range 700°C to 900°C. The equilibrium Laves phase nucleated heterogeneously at grain boundaries and in the matrix [Fig. 3(a)].

Fig. 3. Precipitate structures developed on ausaging austenitic Fe-Mn: (a) after homogenization; (b) after homogenization plus 50% cold work.

(XBB 771-158)

The maximum hardening increment to the yield strength provided by the Laves phase precipitates is about 10 ksi for the Fe-20Mn-2Ti alloy and about 5 ksi for the Fe-28Mn-2Ti alloy.

In order to introduce efficient nucleation sites for precipitation the alloys were cold rolled ~50% between the solution annealing and the aging processes. A large number of very fine precipitates formed randomly in the matrices within a short aging period (~1 hour) [Fig. 3(b)]. A 75 ksi increase in yield strength was obtained in the Fe-20Mn-2Ti and a 65 ksi increase in the Fe-28Mn-2Ti alloy. The enhancement of mechanical properties is due to the randomly distributed precipitates combined with the high defect density and substructure. Approximately 20% uniform elongation was observed in the tensile tests. This ductility results from strain-induced transformation. A $\gamma \rightarrow \epsilon$ transformation occurred in the Fe-28Mn-2Ti alloy while a $\gamma \rightarrow \alpha'$ transformation was predominant in the Fe-20Mn-2Ti alloy.

7. AUSTENITIC ALLOYS FOR RETAINING RINGS IN ELECTRICAL GENERATORS

S. Jin, D. Klahn, G. Thomas and J. W. Morris, Jr.

The purpose of this project is the development of an alloy to be used in making retaining rings

for large electrical generators. These rings restrain the vector end turns and hence are subjected to high operational hoop stresses. The specific design requirements necessitate an alloy with the following room temperature properties:

- nonmagnetic,
- yield stress of ~200 ksi,
- fracture toughness of $\sim 130 \text{ ksi}\sqrt{\text{in}}$,
- resistant to stress corrosion cracking in hydrogen and water.

The currently used retaining ring alloy, 18Mn-5Cr austenitic steel, is questionable for large generator applications because it is only hardenable to 170 ksi and is susceptible to stress corrosion cracking in damp hydrogen. In addition, the manufacturing of retaining rings from this alloy is complex since peak strength is obtained by cold-expansion, a rather difficult process for large retaining rings.

The approach followed to date has centered on austenitic Fe-Ni alloys which have been strengthened by a combination of precipitation hardening and transformation hardening. Alloy chemistry has been adjusted such that initial ausaging at ~700°C results in a fine dispersion of coherent intermetallic precipitates which strengthen the matrix by impeding dislocation motion. A micrograph of Fe-29Ni-4.3Ti ausaged at 750°C for 30 minutes is shown in Fig. 1. This micrograph

Fig. 1. Precipitation hardened austenite showing the γ' precipitates.

(XBB 759-6637)

reveals a dense distribution of spherical γ' (Ni₃Ti) precipitates in the austenite matrix. Additional strength is imparted to this alloy by transformation hardening. This is done by subjecting the alloy to a martensitic and reverse martensitic transformation. First the alloy is quenched in liquid nitrogen (-196°C). In an Fe-29Ni-4.3Ti alloy this resulted in 70% of the matrix transforming to martensite. This martensite is reverted back to austenite by heating to ~800°C. During the martensitic transformation a dense distribution of dislocations and internal boundaries are generated which remain substantially intact during the reverse transformation due to the pinning effect of the γ' precipitate field. An electron micrograph showing the transformation induced defect structure in Fe-29Ni-4.3Ti is shown in Fig. 2. When the M_s temperature is adjusted properly the martensitic plus reverse-martensitic transformations can add ~20 ksi to the yield stress with no reduction in ductility.

This two stage thermal processing treatment of ausaging plus transformation strengthening has been applied to a number of Fe-Ni base alloys. The yield strengths of two alloys, Fe-33Ni-3Ti and Fe-34Ni-3Ti-0.5Al, at various processing stages are shown in Table 1. These two alloys were strengthened to yield strength of ~175 ksi. Other alloy systems containing small additions of Ta, Mo, V, and B and processed by ausaging and transformation hardening have been recently tested

which give yield stresses in excess of 180 ksi while retaining high fracture toughness values. Additional optimization of the alloy chemistry and thermal processing is underway with the aim of achieving the target properties.

Fig. 2. Reverted austenite showing the lath-like substructure and high density of dislocations. (XBB 759-6631)

Table 1. Yield strengths (0.2 % offset).

	Unit = ksi					
	Annealed	Ausaged*	Ausaged + LN ₂ cool	Fast Rev. 650°C/2 min	Fast Rev. 700°C/2 min	Slow Rev. 700°C/5 min
Fe-33Ni-3Ti	50	144	151	168	170	173
Fe-34Ni-3Ti-0.5Ti	56	158	---	169	171	178

* 750°C/4 hr for Fe-33Ni-3Ti alloy and 720°C/12 hr for Fe-34Ni-3Ti-0.5Al alloy.

8. RESEARCH PLANS FOR CALENDAR YEAR 1977

J. W. Morris, Jr.

Our research plans for 1977 include the following:

(1) We plan to utilize the computer code constructed during 1976 to characterize precipitation and coarsening reactions in the Ising lattice with particular emphasis on dilute solutions under small supersaturation.

(2) We plan to complete the geometric characterization of microstructures generated through nucleation and isotropic growth by

simulating and characterizing the boundary and edge-saturated microstructures.

(3) We plan to complete a theoretical solution for the thermally activated glide of a simple dislocation through point barriers, and to continue studies on dislocation glide through barriers of distributed types and on deformation through the simultaneous motion of interacting dislocations.

(4) We plan to continue research on the low-stress creep of superplastic materials and to use stress relaxation tests to clarify the low temperature mechanical equation of state of simple metals.

(5) We plan to continue research on the mechanism of grain refinement through thermal cycling in Fe-Ni alloys and to use Mössbauer techniques to study the influence of austenite stability on low-temperature toughness.

(6) We shall inaugurate new research on the influence of phase transformations on the cryogenic fracture and fatigue properties of austenitic cryogenic steels. This research project will be carried out in collaboration with the Cryogenics Laboratory at NBS, who have supplied us with initial samples.

(7) We plan to clarify the source of intergranular embrittlement in Fe-Mn alloys through surface analysis studies, and identify chemical and metallurgical techniques for removing this embrittlement.

(8) We plan to inaugurate basic research on the welding of cryogenic steels with particular emphasis on the design of good ferritic weld metal materials. This project will be done in conjunction with industrial laboratories with an interest in welding.

(9) We plan to complete the development of an austenitic alloy which can be thermally processed to outstanding strength and toughness for use in retaining rings on large electrical generators.

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b. Fundamentals of Alloy Design

Earl R. Parker and Victor F. Zackay, Principal Investigators

1. BASIC RESEARCH ON SOLID STATE TRANSFORMATION REACTIONS

a. Basic Investigation of Coherent Precipitate Morphology

John A. Wert

Precipitation of second-phase particles in the matrix phase is perhaps the most common method used to strengthen non-ferrous alloys. In the particular case where the precipitate particles are coherent with the matrix phase, the strengthening effects are primarily due to the strain fields which extend into the matrix phase around the particles. The magnitude and extent of the coherency strain fields depend not only on the atomic species present but also on the morphology of the precipitate particles. It was considered of importance to evaluate quantitatively the role of the various parameters associated with the precipitation process in determining the morphology of coherent, second-phase particles. This quantitative analysis could provide a basis for designing new alloys.

From thermodynamic arguments, the orientation of disk-shaped coherent precipitates in the matrix phase is a function of the anisotropy of the energies associated with the elastic strain fields of the particles and with the precipitate-matrix interface. A study was undertaken to calculate the magnitude of the elastic strain energy of a disk-shaped coherent precipitate. This energy was found to be controlled by the elastic properties of the matrix phase and was thus determined by the alloy system under consideration. The computed orientations which minimize the strain energy agree with experimental observations. The magnitude of the strain energy is considerable and depends on the particular species involved in precipitate formation as well as the elastic properties of the matrix phase.

The research carried out so far has identified some of the parameters which control the morphology of coherent precipitates. Further consideration of the results of this study could lead to the development of additional alloys strengthened by the formation of coherent precipitates. For example, the presence of coherent precipitates is the primary factor contributing to the high-temperature strength of the Ni-based superalloys which have proven to be so useful in applications requiring good creep resistance. Yet, coherent precipitation is not currently in the repertory of methods used to strengthen iron-based alloys. Through further research of this type, it is hoped that additional understanding of this important strengthening mechanism can be attained and that other possibilities for iron-based alloy development can evolve.

b. Basic Investigation of the Bainitic Transformation Kinetics and the Morphology of the Decomposition Products

Ana Maria Llopis

The design of new alloys, or obtaining considerable improvements in the properties of the existing ones, largely involves achieving microstructural control through variations in chemical composition and heat treatment. A basic understanding of the kinetic mechanisms of formation, and reaction product morphologies of the bainite transformation, is essential for further enhancement of technologically-useful steels.

Some commercial tempered martensitic steels have significant amounts of ferrite, upper bainite, and lower bainite (formed during quenching). In these steels, ferrite and upper bainite are generally considered to have detrimental effects on the fracture toughness. However, the properties of lower bainite compare favorably with those of tempered martensite, which is generally considered to be the best kind of microstructure. The nature of the bainite transformation continues to be the subject of debate and controversy (40 years after its discovery).

Recent systematic studies on commercial alloy steels with a rapid magnetometric technique have shown that the various alloying elements affect the kinetics of the bainite reaction differently and in ways not heretofore recognized. The effects of Ni, Cr, Mo, Si, which strongly influence the bainite reaction, were studied.

Commercial steels (e.g., 4340, in which some systematic studies were made) are multicomponent systems. Hence, it is difficult to determine the influence of a particular alloying element on the kinetics. Many possible interactions are involved. More fundamental studies were needed, and these were undertaken. Basic ternary alloys Fe-C-X (X = Ni, Cr, Mo, Mn, Al, Si, Co) have been used in thermodynamic studies of the bainite reaction kinetics. Also, quaternary systems such as Fe-C-Mo-Cr, Fe-C-Ni-Cr, Fe-C-Al-Si, and others are being studied, with the purposes of defining in a quantitative manner the interactive effects of the various elements on the kinetics of the bainite reaction.

This research will eventually lead to a more precise understanding of the kinetics, thermodynamic, chemical, and morphological aspects of the transformation so that control of useful properties can be established and new or improved alloys can be designed from basic principles.

2. BASIC INVESTIGATIONS OF THE RELATIONSHIPS BETWEEN MICROSTRUCTURE AND MECHANICAL PROPERTIES

a. Microstructure-Mechanical Property Relationships in Slowly-Cooled Alloy Steels

Ronald M. Horn

Most investigations of the microstructure-property relationships in ultrahigh-strength steels are undertaken after an initial rapid cooling process which leads to a uniform martensitic microstructure throughout the material. However, slower cooling processes are important because many massive structures are too large for uniform rapid cooling. The present investigation is concerned with identifying and controlling the microstructures of continuously-cooled alloy steels which transform in the bainite temperature range. The objective was to discover the nature of the principles involved in the microstructure-property relationships.

The continuous cooling paths investigated were those which correspond to air-cooled materials of varying thickness. These cooling paths were calculated using numerical techniques. The transformation characteristics and mechanical property studies were undertaken using small specimens cooled at rates that simulated those of thick slabs. This simulation was achieved by matching cooling rates in the specimens with those calculated for slabs of the desired thicknesses.

The transformation characterizations showed that a silicon-modified 4340 steel had very high bainitic hardenability, as was expected from alloy theory considerations. The continuous cooling behavior was much more significantly affected by alloying additions than was the isothermal transformation behavior. The microstructures that were present following cooling contained large amounts of retained austenite in a microstructure displaying a bainite morphology. This structure is shown in Fig. 1 with dark field

Fig. 1. Transmission electron micrographs of the 5 cm thick air cooled 300-M, tempered at 300°C, with the associated diffraction pattern: a) Bright field image showing bainitic structure, b) Dark field image revealing retained austenite morphology.

(XBB 769-8115)

imaging used to show the austenite as white areas. The austenite varied in quantity from 15 to 30 volume percent in the treatments investigated. The mechanical and fracture properties of the slow-cooled material were found to vary with the austenite stability. This stability was influenced by a post-cooling tempering process. If the austenite showed a high degree of stability, as it did following a 300-°C temper treatment for the air-cooled conditions investigated, the properties were found to be excellent.

Fig. 2. Comparison of the normalized yield strength and the fracture toughness with the cooling rate for 300-M. The yield strength is normalized to the oil quenched yield strength, 250 ksi. Rates, determined at 450°C, cover a range of air cooled thickness. (XBL 769-7517)

Figure 2 shows the yield strength, normalized against the quenched and tempered yield strength of 250 ksi, as well as the fracture toughness as a function of cooling rate. The structures containing stable retained austenite gave rise to excellent properties in slow-cooled sections up to four inches in thickness. The slow-cooled material had a yield of 160 ksi, a fracture toughness of 100 ksi-in.^{1/2} and an elongation of 18%. The study has shown that cooling simulation techniques provide a viable approach to investigations into the microstructure-property relationships in continuously cooled steels, and that the specific steel investigated had good thick-section properties after the appropriate treatment. This basic study has provided the foundation for an applied research investigation designed to provide superior thick-wall pressure vessel steels.

b. Effect of Silicon on Stress Corrosion Cracking of High-Strength Steel

Mario Castro-Cedeno and Robert O. Ritchie

Stress corrosion cracking behavior of AISI 4340 and silicon-modified 4340 (300-M) alloy steels have been investigated in distilled water and 3%NaCl salt solution environments using pre-cracked specimens tested under dead-loading. The silicon-

modified steel (300-M) in the quenched and tempered condition, was found to show improved stress corrosion cracking resistance to 4340, both when compared at the maximum yield strength of each steel (i.e., 4340 tempered at 200°C vs. 300-M tempered at 300°C), and at the same yield strength (i.e., 4340 tempered at 300°C vs. 300-M tempered at 470°C). The improvement was seen in the form of lower Stage II crack velocities and not in any variation in the threshold stress intensity, K_{ISCC} , below which stress corrosion cracking cannot be detected (Fig. 3). The effect

the presence of mechanically stable retained austenite can be considered to be decidedly beneficial, particularly in steels with higher silicon content.

c. Influence of Impurity Segregation on Behavior of a High-Strength Steel

Robert O. Ritchie

Interactive effects between hydrogen embrittlement and temper embrittlement were examined in a study of fracture and low growth rate (near-threshold) fatigue crack propagation in 300-M high-strength steel, tested in humid air.¹ The steel was investigated in a unembrittled condition (oil quenched after tempering at 650°C) and temper embrittled condition (step-cooled after tempering at 650°C). The embrittlement led to more than 50% reduction in toughness and a change from a fully-fibrous to a fully-intergranular cracking mode of fracture (Fig. 4). Auger

Fig. 3. Crack propagation rate vs. instantaneous stress intensity curves for AISI 4340 and 300-M steels in different heat-treated conditions. (XBL 764-6726)

of microstructure on stress corrosion cracking was also studied by isothermally transforming 300-M steel below M_s to induce significant amounts of retained austenite. The presence of this retained austenite was found to be extremely beneficial to stress corrosion cracking resistance; Stage II velocities were reduced by an order of magnitude when compared with quenched and tempered steel (without austenite) at the same strength level (Fig. 3). It was postulated that this effect could be traced to a retardation in diffusivity of hydrogen atoms, evolved from crack tip surface reactions with the water environment. Additional effects of silicon were considered in terms of i) the retardation of tempering in silicon-modified steel preventing epsilon carbide from acting as a cathodic site for hydrogen evolution and ii) the more amorphous oxide formed on steels containing silicon. It was concluded that for improved resistance to hydrogen induced cracking in 4340-type steels,

Fig. 4. Fracture surfaces from K_{Ic} specimens showing a) 100% microvoid coalescence in unembrittled material, and b) 100% intergranular cracking in temper embrittled material. (XBB 767-6524)

spectroscopy analysis was utilized to identify the segregation phenomenon involved, and it was concluded that the loss of cohesion at interfaces was a result of the co-segregation of alloying elements (Ni and Mn) and impurity elements (P and Si) to prior austenite grain boundaries. With respect to fatigue crack growth, prior temper embrittlement was seen to give rise to a substantial reduction in resistance to crack

Fig. 5. Variation of fatigue crack growth rate (da/dN) in moist air with alternating stress intensity (ΔK) at $R = 0.05$ and 0.70 for unembrittled and temper embrittled 300-M steel.

ΔK_0 is the threshold stress intensity below which crack propagation cannot be detected. (XBL 764-6728)

propagation, particularly at lower stress intensities (Fig. 5). At intermediate growth rates (10^{-5} to 10^{-3} mm/cycle) propagation rates in both unembrittled and embrittled material were largely similar, and only weakly dependent on the load ratio, consistent with the ductile striation mechanism of growth observed. At near-threshold growth rates ($< 10^{-5}$ to 10^{-6} mm/cycle), embrittled material exhibited significantly higher growth rates, 30% reduction in threshold stress intensity values for crack growth (ΔK_0), and intergranular facets on fatigue fracture surfaces (Fig. 6).

Near-threshold propagation rates (and values of ΔK_0) were also found to be strongly dependent on the load ratio. The results were modeled in terms of the synergistic interaction, at low crack velocities, between impurity atoms, segregated to grain boundaries, and hydrogen atoms, evolved from crack tip surface reactions with water vapor in moist air. It was concluded that heat-treatment practices, which allow segregation of impurity elements to interfaces, can be considered to be particularly detrimental to fatigue crack propagation resistance at low-growth rates, especially in the presence of environments which promote hydrogen-assisted cracking.

1. Robert O. Ritchie, Influence of Impurity Segregation on Temper Embrittlement and on Slow Fatigue Crack Growth and Threshold Behavior in 300-M High-Strength Steel, submitted to Met. Trans. A, LBL-5498, October 1976.

d. Influence of Retained Austenite on Tempered Martensite Embrittlement in Ultra-High-Strength Steels

Robert O. Ritchie and Ronald M. Horn

Fracture and mechanical properties were determined for aircraft-quality 4340 and silicon-modified 4340 (300-M) alloy steels, using both conventional (quenched and tempered) and non-conventional heat treatments (air-cooled and

Fig. 6. Morphology of fatigue fracture at near-threshold crack growth rates at $\Delta K = 95 \text{ MPa}\sqrt{\text{m}}$ ($R = 0.05$) in 300-M steel showing (a) ductile transgranular mechanism in unembrittled material and (b) segments of intergranular fracture (I) in temper embrittled material (arrow indicates general direction of crack propagation).

(XBB 764-3784)

isothermally transformed) in an attempt to evaluate the effect of microstructure on tempered martensite embrittlement, i.e., the loss in toughness observed in as-transformed alloy steels when tempered in the range 250-400°C. Microstructural features, particularly carbide and retained austenite morphology, were studied to evaluate their influence on toughness (Charpy and K_{IC}), using transmission electron microscopy. The amounts and mechanical stability (with respect to deformation) of retained austenite were determined using magnetic saturation and x-ray measurements. After tempering in the embrittlement range, it was found that the retained austenite was extremely unstable, concurrent with carbide precipitation between martensite laths. The influence of silicon modification to 4340 was seen to delay the onset of embrittlement (i.e., embrittlement occurred around 275°C in 4340 and 400°C in 300-M), coincident again with the temperature at which interlath carbide precipitation and a corresponding loss in retained austenite stability occurred. The extent of toughness degradation appeared directly linked to the amount of unstable austenite present. It was concluded that, although the mechanism of tempered martensite embrittlement can be traced primarily to carbide precipitation and impurity segregation effects, in steels where significant amounts of retained austenite are present, the loss in toughness due to strain-induced austenite transformation can be substantial.

e. Influence of the TRIP Phenomenon on the Toughness of Heat Treatable Alloy Steels

Gabriel Kohn

Heheman¹ and Babu² among others have shown that substantial amounts of austenite can be retained in AISI 4340 type steels when they are isothermally transformed at temperatures near the M_s . It was also shown that additions of alloying elements, especially Si, increase the amount of untransformed austenite retained at room temperature after cooling from the isothermal transformation temperature.

The main objective of the present investigation was to study the behavior of retained austenite under stress and strain in modified AISI 43XX-type steels and to examine whether it is possible to incorporate the good properties of the TRIP steels in these alloys.

The base steel chosen was AISI 4330 and it was modified with 1.0, 2.0, and 3.0 wt%Si. All the specimens were austenitized for one hour at 900°C and then either oil quenched or transformed isothermally in molten salt at temperatures both above the M_s temperature (350°C) and below it (250 and 200°C).

Isothermal transformation above the M_s (300°C), i.e., at 350°C resulted in steels having various levels of retained austenite. The higher the amount of silicon in the steel the higher was the amount of retained austenite in the form of thin films between the bainite or martensite laths. The mechanical properties of the steels

transformed at 350°C were characterized by low yield strengths ranging from 140 to 180 ksi and moderate ultimate strengths in the range of 200 to 220 ksi. The ductility increased with increasing amounts of retained austenite while the plane strain fracture toughness decreased as the amount of austenite increased. The dominant mode of fracture in all the modified steels was quasi-cleavage thereby reflecting the detrimental effect on toughness of the carbon-enriched retained austenite which transformed, during testing, to martensite. Isothermally transforming the steels at temperatures below their M_s temperature did not change the morphology of the austenite. The amount of the austenite and its carbon content, however, decreased with the decrease in isothermal transformation temperature.

A marked improvement in properties was observed at the lower isothermal transformation temperatures, accompanied by a change in the mode of fracture from mainly quasi-cleavage for steels transformed at the higher temperature to mainly dimpled rupture for steels transformed at the lower temperature. This change was attributed to two factors, the introduction of martensite in the microstructure, and the beneficial effect of the transformation of the lower carbon austenite during testing.

A selected number of experimental results obtained in the present investigation are plotted in Fig. 7. This figure shows the bands of toughness vs. ultimate strength for several steels. It is seen that the strength-toughness combination of steels in the present investigation compared favorably with those of the expensive maraging steels.

Fig. 7. Plane strain fracture toughness vs. ultimate tensile strength for AISI 4330 steel with Si additions and for some other HSLA steels (AISI 4340 + Al and AISI 4340 + Al and Si are from Ref. 3). (XBL 769-7498)

1. R. F. Hehmann, Phase Transformations (American Society for Metals, Ohio, 1970), p. 409.

2. B. N. P. Babu, An Investigation of Bainite Transformation in Medium Carbon Low Alloy Steels, (D. Eng. thesis), LBL-2772, August 1974.
3. M. S. Bhat, research in progress, Lawrence Berkeley Laboratory, Berkeley, Ca.

3. NEW ALLOY DEVELOPMENTS

a. Synergistic Effects of Alloying Elements on Tempering Reactions Involving Austenite Decomposition

M. S. Bhat

The synergistic effect of small amounts of aluminum and silicon added to 4340 steel was determined. Theoretical considerations indicated that these additions would lead to an improvement in mechanical properties because of their effects on the kinetics of the solid-state reactions that occur. This was found to be true.

The process of tempering quenched steels can drastically alter microstructure, and thus affect the mechanical properties. Small amounts of alloying elements can affect the process of tempering and thus provide a means for controlling microstructure and mechanical properties. The precipitation of cementite (Fe_3C) and its agglomeration is classified as the third stage of tempering and occurs in the temperature range of 250°C to 700°C. At the lower temperature end of this stage (250°C to 400°C) an embrittlement of the steel occurs which is referred to in the literature as "500°F embrittlement." The phenomenon is believed to be associated with a critical carbide morphology present when cementite first forms. It is caused by films of carbides which precipitate at martensite lath boundaries. In addition to the embrittlement, there is a severe loss in strength because of the depletion of carbon from the matrix. This stage of tempering is undesirable.

One way of preventing 500°F embrittlement is by the addition of an alloying element which suppresses the formation and retards the growth of cementite at the lower tempering temperatures. It is possible to achieve this goal by controlling the activity of carbon in ferrite. One of the elements which strongly affects the carbon activity is silicon (Si raises the carbon activity). It has been shown that the presence of Si in steel inhibits the formation and growth of cementite at lower tempering temperatures (200°C to 350°C) where lath boundary films form. The consequence of this effect is that the temperature range of cementite formation is elevated and the drastic drop in strength is eliminated. Another element which theory indicates should behave like Si is Al. The Fe-Al and Fe-Si phase diagrams are similar at the Fe-rich end and both these elements are non-carbide formers.

The effect of Al on the tempering behavior of AISI 4340 was found to be similar to that of Si as is shown in Fig. 1. With increasing amounts of Al in the steel, the hardness was retained

Fig. 1. Plot of hardness vs. tempering temperature of AISI 4340 and AISI 4340 + Al steels. (XBL 761-6106A)

to higher tempering temperatures. On studying the microstructure using transmission microscopy, it was found that the microstructural features present in a steel modified with either Al or combinations of Al and Si following tempering at 300°C were (as shown in Fig. 2):

Fig. 2. Electron micrograph showing precipitation of carbides in AISI 4340 + 1.5Al + 1.5Si austenitized at 950°C, quenched and tempered at 300°C. (XBB 761-6374)

1. Dislocated lath martensite (small amounts of twinning were observed),
2. Retained austenite films at lath boundaries,
3. Carbides in some laths (the structure of these carbides has not been identified yet, but the plates appear to lie on planes other than (110) or (100), which are the habit planes of cementite and epsilon-carbide, respectively).

The mechanical properties of AISI 4340 containing 1.5 wt%Al + 1.5 wt%Si are shown in Fig. 3.

Fig. 3. Plot of tensile properties (UTS and YS) and fracture toughness of AISI 4340 and AISI 4340 + 1.5Al + 1.5Si steels. (XBL 762-6525)

The modified steel had yield and ultimate strengths which were higher than those of commercial 4340 steel (following tempering at 300°C). The plane strain fracture toughness (K_{IC}) was increased by about 33%.

b. Research on a New Nickel-Free Stainless Steel

Larry D. Thompson

This research is being conducted to provide the basis for a new class of stainless steels that contain smaller amounts of nickel and chromium than the commercial products. The alloy systems being investigated contain moderate amounts of manganese and chromium, and zero nickel. These alloys utilize the austenitizing ability of manganese, an element which is far cheaper and more accessible than nickel; also there is a significant reduction in chromium content.

The effects of alloying additions of molybdenum, silicon, and copper are also being investigated. These elements are expected to improve the general corrosion resistance. Nitrogen is added to these steels to further stabilize the austenite.

These potential replacement alloys have mechanical properties and corrosion behavior comparable to the commercial austenitic stainless steels. Preliminary results suggest that the Fe-Mn-Cr-base system is a promising system. Yield strengths of 40 to 65 ksi, ultimate tensile strengths of 95 to 125 ksi, reduction of areas of 60 to 85%, and elongations (one-inch gage length) in the range of 60 to 80% have been obtained. Preliminary corrosion data are comparable to those obtained on commercial stabilized austenitic grade, 347SS.

c. The Mechanical Properties of an Isothermally Transformed High-Strength Steel

Thomas A. Lechtenberg

Previous studies of the group suggest that a mixed microstructure of martensite and bainite may be associated with fracture properties superior to those of a standard microstructure with tempered martensite, especially in high carbon steels. To test this prediction, the microstructure of 300-M steel was varied by isothermally transforming it at 325°C, 350°C, 375°C, for times varying up to an hour. The mechanical properties were then determined.

It was found that the fracture toughness, K_{IC} , tended to reach a peak after a short time (8 to 14 minutes) and then to decrease slowly with time for all tempering temperatures. There was a rise with time and temperature in the percentage of retained austenite (determined by x-ray techniques) and a corresponding decrease in the yield strength. However, when yield strength is plotted vs. the fracture toughness, there is no clear correlation (Fig. 4). Using a magnetic saturation technique

Fig. 4. Yield strength vs. fracture toughness. (XBL 773-5203)

which measures the stability of the retained austenite in a uniaxial tension test, the values of percent retained austenite transformed at 0.2% strain and 4% strain were obtained. Again, there was no clear correlation between yield strength and percent retained austenite to 0.2% strain.

However, there appeared to be a qualitative correlation for the austenite transformed at 4% strain (Fig. 5). This data is not inconsistent

Fig. 5. Fracture toughness vs. percent retained austenite transformed at 4% strain. (XBL 773-5202)

with the suggestion of other investigations that the stability of the austenite may influence the toughness of the material as a crack moves through. The Charpy impact energies show a similar rise and same decrease (as the K_{IC} data). The fracture modes were established to be mainly dimple rupture and quasi-cleavage for the higher toughness values (shorter times and therefore more stable austenite) and quasi-cleavage facets for the lower values (less stable austenite).

d. Mechanical Properties of Electroslag Refined 300-M Steel

Thomas A. Lechtenberg

The electroslag process consists of a secondary remelting of metals under a slag cover which produces a fine distribution of slag inclusions and a very low sulfur content (< 0.002%). The effect of the changed inclusion morphology and chemistry on the transverse and longitudinal fracture properties is being investigated. The transverse fracture toughness of the ESR steel has been reported to be better than that of steel melted by the more common vacuum arc remelted (VAR) process. In this study the fracture toughness of ESR 300-M steel is compared to that of VAR 300-M steel.

The plane strain fracture toughness data for ESR and VAR material in the longitudinal orientation is shown in Fig. 6. The inset in Fig. 6 shows the percent retained austenite as determined by x-ray methods at various tempering temperatures. Similar data for the transverse orientation is shown in Fig. 7. These data show that in the tempering temperature range of 350°C to 500°C the fracture toughness of the ESR steel

Fig. 6. Longitudinal fracture toughness vs. tempering temperature. (XBL 773-5204)

Fig. 7. Transverse fracture vs. tempering temperature. (XBL 773-5205)

is equal to or somewhat better in both the longitudinal and transverse orientations. This slight improvement is clearly exhibited when comparisons are made at the same strength levels.

It is planned to examine the behavior of retained austenite in ESR steels using the magnetic

saturation technique developed at this laboratory. Future investigations will include studies of the fracture surfaces as well as the morphological differences of steels made by the two melting processes.

e. Microstructure-Mechanical Property Relationships in an Interphase Precipitation-Strengthened Steel

Yoshinao Mishima

This investigation is directed toward determining the microstructure-mechanical property relationships in steel systems which rely on interphase precipitation for strengthening. Basic studies by Honeycombe et al.¹ on Fe-V-C type steels indicate that these systems might have useful applications. They showed that the austenite of a Fe-0.2C-1V alloy decomposed eutectoidally from the austenite phase into a ferrite-vanadium carbide mixture by interphase precipitation when transformed either isothermally or continuously (see Fig. 8). The isothermal

Fig. 8. TTT diagram for 0.9 w/oV-0.2 w/oC steel. (XBL 773-5206)

transformation characteristics obtained in this study support the contention of Honeycombe et al. These authors also showed that the resulting structure is not the well-known lamellar pearlite, but rather is a fine dispersion of spherical vanadium carbide particles in ferrite. This microstructure is associated with good strength and ductility.

The initial work in this research project has been directed toward determining: (1) processing parameters; and (2) mechanical property-microstructure relationships in a 3Ni-1V-0.2C steel. The nickel addition was made to shift the transformation "C"-curve to a lower temperature range so as to ensure the development of a finely dispersed carbide over a wide range of cooling rates.

Dilatometer studies were made to investigate transformation characteristics for various

computer-determined cooling rates² which correspond to rates of cooling for plates of different section sizes. It was found that: (1) high austenitizing temperature (1100°C ~ 1200°C) are necessary to dissolve the carbides; (2) different transformation rates lead to similar hardness and microstructural appearance; and (3) transformation start temperatures are about 500°C after a 1200°C austenitization treatment. Electron microscopy investigations reveal a fine precipitate in material cooled at a rate equivalent to an air-cooled one-inch slab. Fracture-microstructure relationships will be determined for several cooling rates.

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2. R. Horn, Ph.D. thesis, to be published.

4. EROSION-CORROSION INVESTIGATIONS

a. Effects of Microstructure of Solid Particle Erosion-Resistance of Ductile Alloys

Lorin L. Brass

The purpose of this program is to determine the effects of microstructure on the solid particle erosion of ductile alloys. The material chosen for the first phase of this study was a plain carbon 1075 steel. The steel was heat-treated to three different morphologies: coarse pearlite, fine pearlite, and a spheroidized structure. The material was then subjected to room temperature erosion with 230 micron SiC at velocities of 100 and 200 feet per second. Angles of impingement used were 15°, 30°, and 90°.

The room temperature rate of erosion at a particle velocity of 100 ft/sec increased from a low initial rate to a higher steady-state rate, see Fig. 1. When the velocity of the particles was changed to 200 feet per second the lower threshold region (of the erosion rate vs. grams of impacting particles curve) was moved to the left. It was also observed that the spheroidized structure (RB88) was the most erosion-resistant, although it was slightly softer than the coarse pearlite (RB90) and much softer than the fine pearlite (RB99). These results indicate that erosion is not a function of hardness only and that the microstructure of the material plays a significant role in the erosion mechanism process.

Single particle impact studies at 100 feet per second velocity show that the spheroidized structure is severely plastically deformed at the surface early in the erosion process with a plowing type of deformation which yields large material displacement with little material loss. As the material deforms and work hardens upon exposure to additional particle impacts, microcracking was observed to take place near the carbide particles below the surface, Fig. 2. Coalescence of these cracks results in material loss and accounts for the increased erosion rate in Fig. 1.

Fig. 1. Erosion rate vs. grams of impact particles. Fine pearlite 100 ft/sec + 65-60 mesh SiC. (XBL 769-10487)

Fig. 2. Spheriodized 1075 steel. Transverse cross section + 65-60 mesh S.C. (or 230 μm), 200 fps, 30° angle of impingement. (XBB 7612-11369)

The pearlitic structures do not show such microcracking below the surface, but rather crack

more severely at the impacted surface. This results in less material displacement prior to loss of material and consequently to greater weight losses.

b. Sulfidation of SAE 310 Stainless Steel

D. B. Rao

The internal components of a coal gasifier are exposed to extremely hostile environments having high sulfur partial pressures (dependent upon the sulfur content of the coal) at elevated temperatures (900 K to 1300 K). Realizing that sulfur can cause severe corrosion problems, the sulfidation properties of one of the candidate materials (SAE 310 stainless steel) have been studied as a function of sulfur partial pressure and temperature.

At a fixed temperature of 1965 K, the sulfidation kinetics, composition, and morphology of sulfide scale formation were studied over a range of sulfur potentials from $1.5 \times 10^{-4} \text{ Nm}^{-2}$ to $9 \times 10^{-4} \text{ Nm}^{-2}$. At all sulfur potentials investigated, the sulfide scales were found to be multilayered. The outer layer consists of Fe-Ni-S, the middle layer consists of a mixed thiospinel of variable composition, $\text{Fe}(\text{Fe}_{2-x}\text{Cr}_x\text{S}_4)$, and the inner layer consists of dispersed sulfides (rich in chromium) in a metal matrix (nickel and iron). The relative thickness of the individual layers as well as the composition was found to depend on the sulfur potential. The outer layer thickness progressively decreased as the sulfur potential decreased whereas the middle layer thickness increased and the inner layer thickness remained essentially constant. At very low sulfur potentials the outer layer disappeared completely, as is shown in Fig. 3. Finally, at high temperatures (1145 K) where the conditions are favorable for the formation of an outer layer, the outer layer became a liquid and the melt separated into a two-phase solid upon cooling, as shown in Fig. 4a. The grey phase in this figure is the iron-nickel sulfide and the bright phase is a metallic phase of iron and nickel. In Fig. 4b all the three layers are shown and in Fig. 4c the inner layer structure is shown in more detail.

At all sulfur potentials investigated the reaction rate was found to obey a parabolic rate law after an initial transient period. Extended transient periods could be attributed to unsteady state conditions resulting from compositional variations in the middle layer. The growth of the outer layers was found to be primarily due to the transport of cations whereas the inner layer growth was due to the dissociation of the primary product at the alloy scale interface and was dependent on the activity of chromium. The overall rate controlling step was found to be the diffusion of metal ions through the middle layer.

Fig. 3. Influence of sulfur pressure at 1065 K.

(XBB 773-1646)

Fig. 4. Layers of sulfide scale. T = 1145 K;
 $P_{S_2} = 1.2 \times 10^{-2}$; t = 3.75 h. (XBB 773-1647)

c. Pourbaix Stability Diagram Development for Stainless Steels in Coal Gasifier Environments

Bruce A. Gordon

Much of the work being expended in the area of high-temperature corrosion of alloys is being done without the aid of good theoretical models. In the early phases of this study some theoretical predictions of the corrosion behavior of 310 stainless steel were made for oxidizing/sulfidizing environments. These studies are a prelude to a later investigation of the erosion-corrosion behavior of this steel.

As a starting point for a theoretical model of corrosion, the equilibrium behavior of 310 stainless steel in a sulfur-oxygen environment must be considered. Pourbaix stability diagrams relating metal-scale equilibria as a function of gas-phase partial pressures have been known for some time but their use has been restricted to that of pure metals, or, at most, binary alloys. In this work, Pourbaix-style stability diagrams for the Fe-Ni-Cr-S-O system were made using literature data for the non-ideal behavior of the components in the alloy.^{1,2} Because the features of these diagrams change with temperature, the operating temperature of a typical coal gasifier (1227 K for the Synthane System gasifier) was chosen and the diagram (see Fig. 5) was constructed from those for the individual alloy constituents. When these are superposed on one diagram, it is possible to observe what phases will be in thermodynamic equilibrium with the alloy surface and with each other. This enables predictions to be made as to what species might be present in complex technological environments.

Fig. 5. Pourbaix stability diagram for the Fe-Ni-Cr-S-O system at 1227 K. (XBL 766-7122)

Plotted on the figure are the regions in which P_{S_2} and P_{O_2} fall for typical gasification reactors, S for the Synthane process, H for Hygas, and C for Consol. It is noted that at 1227 K (954°C), only the components of the Consol gasifier appear to be free from attack by sulfur, by virtue of a Cr_2O_3 coating. On the other hand, conditions of the other two processes result in the formation of a liquid nickel sulfide phase. These results suggest that the materials that make up these plants should be those that resist degradative sulfidation.³

An object of this investigation is to establish whether these diagrams can be used reliably by design engineers to simplify the problem of predicting what solid phases are likely to be encountered in plant designs.

1. N. F. Mazandarany and R. D. Pehlke, Met. Trans. 4, 2067 (1973).
2. G. R. Belton and R. J. Fruehan, Met. Trans. 1, 781 (1970).
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d. Solid Particle Flow in Entrained Gas Streams

D. Kleist

The purpose of this project was to develop a computer program which would predict the velocity of solid particles in a one-dimensional entrained gas flow as a function of the differential pressure across the nozzle in which the gas-particle mixture flowed. The velocity of the particles was to be predicted as a function of the variables presented in Fig. 6. The conditions selected for the flow analysis represent those of solid particles of coal, char, and ash in a coal gasification system.

CAPABILITY: TO PREDICT PARTICLE FLOW VELOCITIES ENTRAINED IN A ONE DIMENSIONAL GAS FLOW

BASIC CONSIDERATIONS INCORPORATED:

GAS FLOW: EQUATIONS OF CONTINUITY, MOMENTUM, ENERGY AND STATE FOR ADIABATIC, COMPRESSIBLE FLOW; WALL FRICTION; HEAT TRANSFER

GAS-PARTICLE FLOW: AERODYNAMIC DRAG FORCES; PARTICLE-GAS MASS FLOW RATIO; PARTICLE TRAJECTORY; ENERGY VARIATIONS

REQUIRED INPUT DATA:

DUCT: DIAMETER, LENGTH, ROUGHNESS, TEMPERATURE

GAS: TEMPERATURE, PRESSURE, THERMAL COND., SPECIFIC HEAT RATIO

PARTICLE: SIZE, DENSITY, LOADING, SPECIFIC HEAT, INITIAL VELOCITY

UTILIZES MULTIPLE ITERATIONS PER LENGTH OF DUCT

GIVES PARTICLE VELOCITY FOR ΔP ACROSS NOZZLE

Fig. 6. One-dimensional flow computer program. (XBL 761-225)

Particles of various sizes, shapes, and densities were experimentally flowed through a constant diameter tube nozzle at room temperature to verify the predicted velocities of the computer program. Test particle velocities were determined using photographic and rotary disk types of particles velocity measuring devices. Excellent correlations were obtained over a range of particle velocities and differential pressures. The developed computer program is being used to determine the equipment settings for devices being used to determine the erosion behavior of metals for use in coal gasification equipment.

e. Erosion Deformation Mechanisms in Alloys

D. McFadden

The purpose of this project was to relate the results and observations of solid particle erosion experiments on ductile metals to different erosion theories which have been proposed. To achieve the desired correlations between the proposed theories and these experiments, both single and multiple particle impact tests were used.

The single particle tests were conducted to provide insight into the erosion mechanisms. Finnie's cutting theory of erosion^{1,2} was found to model the erosion process occurring at low angles. The scanning electron microscope photographs of individual particle impacts ($10 < \alpha < 30$) show a cutting process taking place. Profiles taken of these impacts compared favorably with the predicted profiles generated from Finnie's analysis, Fig. 7. With the photographs and profiles, many of the assumptions used in the cutting analysis were shown to be true. For the region of the angle α , the particles' angle

Fig. 7. Scanning electron micrograph showing cutting by individual particle impact ($10 < \alpha < 30$) and the corresponding surface profile. (XBB 761-581)

of attack, between 30 and 60° , the erosion process was found to be a combination of cutting and ploughing action. No erosion theory was found to be applicable to this region ($30^\circ < \alpha < 60^\circ$). The region of α between 60° and 90° was found to conform to a "dynamic" hardness theory of erosion as proposed by G. Sheldon.⁵ Sheldon's analysis agreed with many of the single particle impact results.

Multiple particle erosion tests were conducted to determine the applicability of single particle theories. It was found that Finnie's analysis

was the only theory which predicts the shape of the erosion curve for α less than 40° . The experimental results showed the multiple particle erosion process was independent of the particle velocity, that the velocity exponents (erosion $\propto v^n$) were a function of the angle α and surface roughness, and that the thermal properties of the targets used in metal cutting theories had little effect on the velocity exponent. It was found that no theories could predict multiple particle erosion for the higher angles ($40^\circ < \alpha < 90^\circ$) of particle incidence.

1. I. Finnie, Erosion of Surfaces by Solid Particles, *Wear* 3, 87 (1960).
2. I. Finnie, Some Observations on the Erosion of Ductile Metals, *Wear* 19, 81 (1972).
3. S. Sheldon, private communication (1975).

5. CONTINUUM MECHANICS PROJECTS

a. Effects of Microstructure and Load Ratio on Fatigue Crack Propagation in Ultra-High-Strength Steel

Robert O. Ritchie

Fatigue crack propagation behavior of an ultra-high-strength steel (300-M) has been investigated in humid air over a very wide spectrum of growth rates from 10^{-8} to 10^{-1} mm/cycle. Particular emphasis has been devoted to the influence of mean stress (or load ratio $R = K_{\min}/K_{\max}$) and microstructure on fatigue crack growth near the threshold stress intensity for crack propagation, ΔK_0 . Increasing the load ratio from $R = 0.05$ to 0.70 was found to lead to increased near-threshold growth rates, and a decrease in the threshold stress intensity. Similarly, increasing material strength, by varying the microstructure through quenching and tempering and isothermal transformation, resulted in higher near-threshold growth rates, and a marked reduction in ΔK_0 (Fig. 1). Increasing the prior austenite grain

Fig. 1. Variation of fatigue growth rate (da/dN) with alternating stress intensity (ΔK_0) at $R=0.05$, for 300-M steel, quenched and tempered between 100°C and 650°C . (XBL 764-6727)

size, on the other hand, did not change the threshold, but resulted in lower near-threshold crack propagation rates.¹ Such effects were not observed at higher growth rates. By performing cyclic stress-strain tests, the influence of strength on ΔK_0 was rationalized in terms of the cyclic hardening or softening response of the material, and hence it was shown that cyclic softening and coarsening the microstructure can be beneficial to fatigue crack propagation resistance at very low growth rates.

A model² was developed to account for the effect of strength and load ratio on the threshold stress intensity, ΔK_0 , in steels, based on a critical fracture stress criterion for crack growth modified by the influence of hydrogen, evolved by crack tip surface reactions with water vapor in moist air. The model is shown to correctly reproduce the observed trend (Fig. 2)

Fig. 2. Summary of results showing variation of threshold for fatigue crack growth (ΔK_0) at $R=0$ with yield strength for steels. Solid lines from threshold model. (XBL 764-6722A)

of increasing threshold ΔK_0 values with decrease in strength for steels, and is consistent with observed effects of grain size¹ and impurity effects^{3,4} on near-threshold fatigue crack propagation.

1. R. O. Ritchie, Effects of Strength and Grain Size on Near-Threshold Fatigue Crack Growth in Ultra-High-Strength Steel, Proceedings of 4th Int. Conf. on Fracture, Waterloo, Canada, June 1977, LBL-5188, June 1976.
2. R. O. Ritchie, Near-Threshold Fatigue Crack Propagation in Ultra-High-Strength Steel: Influence of Load Ratio and Cyclic Strength, submitted to J. Eng. Mats. and Tech., Trans. ASME, Series H, 1976, LBL-5496, October 1976.
3. R. O. Ritchie, Influence of Impurity Segregation on Temper Embrittlement and on Slow Fatigue Crack Growth and Threshold Behavior in 300-M High Strength Steel, submitted to Meta. Trans. A, LBL-5498, October 1976.

4. R. O. Ritchie, Effects of Microstructure on Near-Threshold Fatigue Crack Propagation in Ultra-High-Strength Steels, Proceedings of the Metals Society Conference, Fatigue 1977, Cambridge, U.K., March 1977, LBL-5730, March 1976.

b. Comparison of Toughness Evaluation of High-Strength Steel by Charpy and K_{IC} Tests

Robert O. Ritchie

It has been shown for as-quenched AISI 4340 alloy steels¹ and similar low-alloy steels^{1,2} that high austenitizing temperatures at 1200°C, instead of conventional heat-treatment at 870°C, can result in an increase in fracture toughness, K_{IC} , but a decrease in Charpy V-notch impact energy, without change in strength. The effect was further examined for as-quenched and quenched and tempered (at 200°C) 4340 steel austenitized at 870, 1000, 1100, and 1200°C in an attempt i) to find an explanation for this behavior consistent with other mechanical properties and ii) determine the optimum austenitizing treatment for this steel. By performing radius notched (Fig. 3) and sharp-cracked toughness (Fig. 4) tests under both states [K_{IC} and dynamic (K_I)] the effect of increasing austenitizing temperature was related to the coarsening of microstructure at higher temperatures, specifically to an increase in prior austenitic grain size (for stress-controlled fracture) and an increase in particle spacings (for strain-controlled fracture). The corresponding decrease in rounded-notch toughness (e.g., Charpy) was consistent with a decrease in fracture stress (for stress-controlled fracture) and a decrease in uniaxial and plane

Fig. 3. Variation of absorbed energy vs. austenitizing temperature of as quenched AISI 4340 steel. Also shown is the area under the σ/ϵ curve. (XBL 766-7077A)

Fig. 4. Variation of static (K_{IC}) and dynamic (K_{ID}) fracture toughness with austenitizing temperature of as quenched AISI 4340 steel. (XBL 764-6725A)

strain ductility (for strain-controlled fracture). It was concluded from this study that, i) the optimum austenitizing temperature for AISI 4340 steel should be between 1000 to 1100°C, and ii) that assessment of toughness in alloy design studies should include both rounded-notched and sharp-cracked tests.

1. R. O. Ritchie, B. Francis and W. L. Server, Evaluation of Toughness in AISI 4340 Steel Austenitized at Low and High Temperatures, *Met. Trans. A*, 7 831 (1976) (LBL-4235, Sept. 1975).
2. M. F. Carlson, B. V. N. Rao, R. O. Ritchie, and G. Thomas, Improvements in Strength and Toughness of Experimental Fe/Cr/C Type Steels, *Proc. 4th Int. Conf. on the Strength of Metals and Alloys*, Nancy, France, Aug./Sept. 1976 (LBL-5111, May 1976).

c. Electrical Potential Technique for Crack Initiation Measurement in Fracture Toughness Testing

Robert O. Ritchie

The extension of linear elastic fracture mechanics to evaluation of the toughness of lower strength materials has led to the formulation of several parameters to measure toughness under elastic-plastic conditions. Such parameters, e.g., crack opening displacement and J-constant integral, require measurement at fracture initiation, which, under nonlinear elastic conditions, may not be coincident with final catastrophic failure. At present, the techniques used to identify initiation involve multi-specimen testing using an R-curve analysis. In an attempt to provide a single specimen test technique, this study is examining the feasibility of using the electrical potential technique as a means of measuring resistance changes within a test specimen at the onset of slow crack growth. Effects of elastic and plastic deformation, yield strength, fracture surface roughness and crack closure are being examined for their influence on the change in potential with increasing load,

such that unambiguous criteria can be set for the variation in potential at crack initiation.

6. RESEARCH PLANS FOR CALENDAR YEAR 1977

Earl R. Parker and Victor F. Zackay

In the six months since the formation of ATOM, every effort has been made to relate, wherever possible and desirable, the basic and the applied aspects of the materials research group. As part of this effort, several major projects in the basic area have been completed and new ones instituted in their place. Brief descriptions of several of these are given below.

A major investigation will be made of the fundamentals of the abrasion-resistance of metals. The provocative theories, recently enunciated by Professor N. Suh of MIT will serve as a guide to the structuring of the program in its initial phases. Efforts will be made to delineate the important metallurgical and mechanical variables and to develop a definitive test for abrasive wear. The basic understanding gained from this investigation will be channeled into the applied aspects of the Fossil Energy project on the development of wear-resistant alloys for coal handling and for components in coal gasifiers.

The erosion and corrosion project will continue to be one of the largest of the group. In the past year the effort has largely been confined to room temperature experimental studies. These included the hydrodynamics of gas-particle flow and the role of specimen microstructure in resisting erosive wear. Basic investigations were also made of the behavior of Fe-Ni alloys in relatively simple chemical environments. In the coming year extensive investigations of erosion and corrosion at elevated temperatures and in more complex chemical environments will be conducted. The basic results of this project should be applicable to the applied research on the development of sulfidation-resistant alloys for coal gasifiers (Fossil Energy Research).

7. 1976 PUBLICATIONS AND REPORTS

Earl R. Parker, Victor F. Zackay, and Associates

Papers Published

1. B. N. P. Babu, M. S. Bhat, E. R. Parker, and V. F. Zackay, A Rapid Magnetometric Technique to Plot Isothermal Transformation Diagram, *Met. Trans. 7A*, 17 (1976).
2. V. F. Zackay and E. R. Parker, The Changing Role of Metastable Austenite in the Design of Alloys, *Annual Rev. of Materials Sci.* 6, 139 (1976).
3. V. F. Zackay, Fundamental Considerations in the Design of Ferrous Alloys, *Alloy Design for Fatigue and Fracture Resistance*, AGARD-CP-185, pp. 5-1 to 5-20, January 1976.

4. V. F. Zackay, What We Don't Know About Thermomechanical Processing, Materials Science and Engineering, 25, 247 (1976).

5. B. Francis, Increasing the Fracture Toughness of A Maraging Steel Type Alloy, Met. Trans. 7A, 465 (1976).

6. M. D. Bhandarkar, M. S. Bhat, V. F. Zackay, and E. R. Parker, Met. Trans. 7A, 753 (1976).

7. C. E. Ericksson, M. S. Bhat, E. R. Parker, V. F. Zackay, Isothermal Studies of Bainitic and Martensitic Transformation in Some Low Alloy Steels, Met. Trans. 7A, 1800 (1976).

8. T. C. Lindley, C. E. Richards and R. O. Ritchie, Mechanics and Mechanisms of Fatigue Crack Growth in Metals: A Review, Metallurgica and Metals Forming 43, 268 (1976).

9. R. O. Ritchie, M. F. Carlson, B. V. N. Rao, G. Thomas, Improvements in Strength and Toughness of Experimental Fe/Cr/C Type Steels, Proceedings of 4th International Conference on the Strength of Metals and Alloys, Nancy, France (May 1976).

LBL Reports

1. R. O. Ritchie, Near-Threshold Fatigue Crack Propagation in Ultra-High-Strength Steel: Influence of Load Ratio and Cyclic Strength, LBL-5496, Oct. 1976.

2. R. O. Ritchie, B. Francis, and W. L. Server, Further Discussion on the Evaluation of Toughness in AISI 4340 Alloy Steel Austenitized at Low and High Temperatures, LBL-5760, Nov. 1976.

3. R. O. Ritchie, B. Francis, W. L. Server, Evaluation of Toughness in AISI 4340 Alloy Steel Austenitized at Low and High Temperatures, LBL-4125, Sept. 1976.

4. R. O. Ritchie, Influence of Impurity Segregation on Temper Embrittlement and on Slow Fatigue Crack Growth and Threshold Behavior in 300-M High-Strength Steel, LBL-5498, Oct. 1976.

5. R. O. Ritchie, Effects of Strength and Grain Size on Near-Threshold Fatigue Crack Growth in Ultra-High-Strength Steel, LBL-5188, June 1976.

6. R. O. Ritchie, Effects of Microstructure on Near-Threshold Fatigue Crack Propagation in Ultra-High-Strength Steels, LBL-5730, March 1976.

Invited Talks and Papers

The following were delivered by Professor V. F. Zackay at the TMS/AIME Fall Meeting in Niagara Falls, September 20-23, 1976.

1. M. S. Bhat, M. D. Bhandarkar, V. F. Zackay, E. R. Parker, The Influence of Microstructure on the Creep-Rupture Properties of a Laves-Phase Alloy.

2. Ana Maria Llopis, V. F. Zackay and E. R. Parker, Effect of Different Alloying Elements on the Kinetics of the Bainite Reaction.

3. G. T. Haddick, V. F. Zackay and E. R. Parker, Optimization of Strength and Ductility of Fe-Mn TRIP Steels.

4. M. S. Bhat, G. Kohn, E. R. Parker and V. F. Zackay, Microstructure and Mechanical Properties of AISI 4340 Steel Modified with Aluminum and/or Silicon.

5. N. Kar, E. R. Parker, and V. F. Zackay, Interrelationships Between Thermal History and Mechanical Properties of a Secondary Hardening Steel.

6. L. Thompson, V. F. Zackay, and E. R. Parker, An Investigation of the Mechanical and Corrosion Behavior of High Manganese, High Chromium, Iron-Based Alloys.

7. R. Horn, V. F. Zackay and E. R. Parker, An Investigation of the Mechanical and Fracture Properties of Air-Cooled Thick Section 300-M.

8. G. Kohn, M. S. Bhat, V. F. Zackay, and E. R. Parker, Effect of Silicon on the Microstructure and Mechanical Properties of AISI 4340 Steel.

9. R. O. Ritchie, R. Horn, V. F. Zackay and E. R. Parker, The Inconsistency in Toughness Evaluation by Charpy and I_{IC} Tests of AISI 4340 Steel Austenitized at Increasing Temperatures.

c. Relations Between Dislocations, Point Defects, and Properties of Metals

Jack Washburn, Principal Investigator

1. PROGRAM ON RADIATION DAMAGE EFFECTS IN METALS

a. Temperature Dependence of the Threshold Energy for Frenkel Pair Production

R. Drosd

The minimum energy required to produce stable Frenkel pairs during high energy particle irradiation (E_d) is a fundamental parameter of great importance in calculations of atomic displacement rates. Traditionally E_d has been measured at room temperature or below where a value of about 18 eV is found for copper. It has been a common assumption that E_d was almost temperature independent. The potential importance of small changes in E_d is illustrated by the fact that for 650 keV electron irradiation of Cu a reduction of E_d from 20 to 12 eV increases the displacement damage rate by 240%. Our experiments indicate that E_d decreases to about 12 eV in copper at 300 K.

With respect to the temperature dependence of E_d there are two conceptually separate processes of importance. That is (1) Frenkel pair production, and (2) the possibility of subsequent correlated recombination (recombination of a vacancy with its own interstitial). If correlated recombination occurs there is no permanent effect of the displacement.

The mechanism of Frenkel pair production at low energies is generally assumed to be that of focused replacement collisions (FRC). Thermal vibrations will tend to defocus FRC's and hence can only account for an increase in E_d . From theoretical calculations of E_d it can be seen that the lattice parameter and elastic constants are of great importance. At high temperatures both these properties vary in such a manner (they increase and decrease respectively) to lower the value of E_d . However, due to the relatively small changes in these material properties over the temperature ranges studied here, it is not expected that a large decrease in E_d would occur.

The temperature dependence of the probability that Frenkel pairs will suffer correlated recombination arises from the ability of thermal vibrations to separate closely spaced vacancies and interstitials that would annihilate otherwise. Hence less energy is required from the electron-atom collision to produce some freely migrating point defects. We favor this mechanism as most likely to be responsible for the observed decrease in E_d . To determine the generality of this effect we hope to study the temperature dependence of E_d in aluminum. Al is of interest since at room temperature electrons of only 160 keV are required for Frenkel pair production. If a substantial reduction in E_d occurs at elevated temperatures, then it may be possible to produce displacements with 100 keV electrons. This would be of great interest since radiation damage effects could be expected for aluminum alloys even

when observations are being made in standard 100 kV electron microscopes.

b. Subthreshold Displacement Damage in Copper-Aluminum Alloys During Electron Irradiation

R. Drosd

Many investigators have suggested that if impurity atoms, which are lighter than those of the solvent, are present in significant quantities that the measured value of E_d the minimum energy required to displace an atom from its regular site to a great enough distance to form a stable vacancy interstitial pair will become indistinct as well as taking on a somewhat lower value than in the pure metal. For electron bombardment this effect becomes even more pronounced because of the large differences in mass of the two particles involved. E_c , the minimum incident electron energy required to form stable Frenkel pairs, is orders of magnitude higher than E_d . Lighter impurities can absorb energy from a bombarding electron with greater efficiency than the heavier solvent atoms since they are closer in mass to the incident particles. For this reason, light impurities can cause a significant decrease in E_c which may be erroneously interpreted as a decrease in E_d .

Our work has been first to experimentally confirm that light impurities can indeed cause "subthreshold" displacements (displacements arising from incident electrons of energy lower than E_c for the pure metal), and also to determine what impurity concentration would be sufficient to cause measurable effects on E_c . We have studied the Copper-Aluminum system with Al as the impurity atom. The values of E_d and E_c for Cu are 18 eV and 380 keV respectively. Irradiations at 300 keV were carried out on Cu containing 2, 7, and 15 at%Al at 325°C. In all alloys dislocation loops were found to nucleate and grow at the above-mentioned subthreshold voltage. From studies of the dislocation loop growth rates the subthreshold damage cross section was estimated and good agreement was found with theoretical calculations. Hence it was confirmed that light impurity atoms do contribute to "subthreshold" displacements.

Al was used as the impurity for experimental convenience, but light gaseous atoms are of more practical interest. However, for these impurities an interesting paradox arises. Due to their very small mass they can absorb large amounts of energy from the incident electrons, but during a subsequent collision with solvent atoms they can only pass on a small fraction of that energy. This is a result of the fairly large difference in mass of the two atomic species. Therefore extremely light impurities (H, He) will be ineffective in causing subthreshold damage in Cu. This remains to be proven experimentally, however. We hope to confirm this conclusion by studying the Cu-Be system, with Be as the impurity, where

we would expect to find an almost negligible subthreshold damage rate even at fairly large concentrations of Be.

c. Climb of Split Dislocations Due to Preferential Capture of Interstitial Atoms

Thomas Kosel

For the past several years we have been studying the climb of dislocations under conditions that simulate the temperature and point defect concentrations that result in growth of voids and swelling of metals. Dislocations represent a biased sink in that they attract interstitial atoms more strongly than they do vacancies. Therefore, if there are unbiased sinks available such as voids or in our case the surfaces of a thin foil specimen there will be a partial separation of the two kinds of defects. Even though they are created in equal numbers a slight excess of vacancies will go to the voids and a slight excess of interstitials will go to dislocations.

Figure 1 shows a dislocation initially nearly pure screw which climbs into helical shape by this preferential capture of interstitial atoms. Between 4 and 6 minute pictures the helix has grown out to one surface of the foil so that each turn now becomes a separate loop. Some of

the interesting aspects of this kind of dislocation climb in copper that are illustrated by this series are the following:

(1) Climb rate of each segment of a dislocation line is not determined only by the point defect supersaturation that exists in the immediate vicinity of that segment. This is illustrated by the climb rate of segments near the foil surfaces where point defect supersaturation falls to zero but climb rate does not. This requires pipe diffusion, mass transport along the dislocation core.

(2) Dislocations climb so that all segments lie on a {111} plane and therefore retain glide mobility during climb. This means that jog nucleation on a split dislocation is relatively difficult. Note that between the 4 minute and 6 minute pictures the end of the helix has broken away from a pinning dislocation and all the turns have sprung out to larger spacings on the glide cylinder.

(3) The climb rates for dislocations near edge orientation and those near screw orientation are comparable. Although more accurate measurements are necessary this implies that fewer excess interstitials are captured per unit time by a dislocation near screw orientation than by one near edge orientation.

Fig. 1. Helix grown in a pure copper foil; 350 kV; 270°C; 1.10 amps/cm² (i.e. a fairly intense beam); (110) foil. Aside from all the interesting features of the helix, this is a good illustration of the temperature dependence of the threshold energy; the lowest published Cu threshold is about 380 kV. (XBB 767-6025)

(4) This helix was grown at 270°C with an electron beam of 350 kV. It constitutes definite proof that free interstitials and vacancies are produced in pure copper at a threshold energy well below the accepted low temperature threshold of 18 eV.

d. Nucleation of Jogs on Widely Split Dislocation*

Krishna Seshan

The climb of extended dislocations is difficult as extended jog pairs have to be created. The greater the separation of the partials, the slower is the climb rate at small supersaturation.

However, experimental results¹ show that the activation energy for this process of jog formation is much lower than those calculated (~100 eV) based on the model of Hirth and Lothe.

To solve this dilemma a modified process for the formation of jogs has been proposed. First a small loop forms below one of the partials, this dissociates on its glide cylinder, and at a critical size it reacts with the extended dislocation forming an extended jog, Fig. 2.

Fig. 2. Model for jog formation on widely split dislocations. (XBL 761-6302)

We have computed the energy of the intermediate configurations taking into account all the 91 dislocation interactions. The lowest energy configurations for various intermediate sizes are shown in Fig. 3.

Fig. 3. Equilibrium shape of extended jog pair vs. the area S. (XBL 7612-10939)

Here the dislocations are dissociated by a distance of $65b$. The nucleation of a $15b$ loop for instance does not produce the critical dissociation to form the extend jog-pair.

The calculations show that if a loop of diameter h can be nucleated, near a dislocation of dissociation width d , the complete jog pair is

formed when $h \sim d$. The calculations show also that mixed, edge-screw, parts of an extended dislocation should climb more easily than pure edge or pure screw segments.

Lastly, there is a threshold in the supersaturation, above which loops of size ' h ' are easily nucleated, and climb proceeds rapidly. Below this threshold, the nucleation of jogs on dissociated dislocations should be the rate controlling step, which determines the climb rate. This threshold depends on the stacking fault energy.

This last result explains the experimental observation of Tom Kosel (Ph.D. thesis) that below a critical threshold supersaturation, the dislocations stop climbing. This threshold was a function of stacking fault energy as predicted by the above model.

* J. Grilhe, M. Borsson, K. Seshan, and R. J. Grabori, Climb Model of Extended Dislocations in FCC Metals, to be submitted for publication.

1. Tom Kosel, Ph.D. thesis, 1975.
2. J. P. Hirth and J. Lothe, Theory of Dislocation, McGraw Hill, 1968, p. 532.

e. The Effect of Changing Dislocation Density and Void Density on the Swelling of 316 Stainless Steel During Irradiation

Arvind Sirvastava

The swelling vs. displacement per atom (dpa) relationship obtained in the irradiation of 316 stainless steel to 600 dpa by protons at 625°C is shown in Fig. 4. Assuming a homogeneous

Fig. 4. Swelling vs. displacement per atom in 316 stainless steel at 625°C. (XBL 762-6451)

distribution of spherical voids and solving the point defect diffusion equations, the swelling curve in Fig. 4 was explained by assuming the variations in dislocation density and void density shown in Fig. 5. In the very early stages of

Fig. 5. Changes in dislocation density and void density which could account for the swelling curve of Fig. 4. (XBL 764-6772)

irradiation (swelling ~1%) dislocation density and void density are both expected to reach their maximum values by agglomeration of interstitials and vacancies respectively. These maxima correspond to a very low rate of swelling. Beyond the early stages and below about 50% swelling (stage 1, dpa < 200) a slow rise in the rate of swelling up to about 0.8% per dpa is assumed to be caused by a gradual decrease in the dislocation density due to the image force attraction of dislocations toward void surfaces and due to climbing together of dislocations of opposite sign. Coalescence of voids is expected in stage 2 (200 < dpa < 425) due to their increasingly close proximity (~2000Å). The surface area of voids per unit volume remains near optimum for maximum rate of void growth. Finally increasing void volume to the point where all dislocations are within about 500Å of a void surface results in a sharp decline in the dislocation density. All the dislocations must, then, terminate at void surfaces while climbing and gliding during irradiation. The sharp reduction in the rate of swelling in stage 3 (dpa > 425) is thought to be a consequence of this decrease in dislocation density to a value below that necessary for maximum rate of void growth. Void surfaces become the overwhelmingly predominant sink for both interstitials and vacancies.

2. RESEARCH RELATED TO ION IMPLANTATION IN SEMICONDUCTORS

Ion implantation has become a commercially important technique for introduction of dopant elements into silicon. For that reason techniques

are well developed for getting the desired electrical properties. This does not mean however that we have a satisfactory understanding of the events that occur during implantation and at each stage of post-implantation annealing.

For the past several years we have tried to make some systematic observations on the nature and properties of the defects which eventually get big enough for study by transmission electron microscopy. The following sections (a) through (e) are all parts of this continuing effort.

a. Characterization of Rod-like Defects in Boron Implanted Silicon by Diffraction Contrast Analysis

Wei-Kuo Wu

Two kinds of rod-shaped defects formed during post-implantation annealing of silicon which has been implanted with boron ions to a dose ($2 \times 10^{-4}/\text{cm}^2$) have been identified by contrast analysis of transmission electron micrographs.

All rods initially have a long axis along a $\langle 110 \rangle$ direction. From the contrast analysis, it has been concluded that one set can best be described as elongated imperfect (Frank) dislocation loops or dipoles on $\{111\}$ planes with Burgers vector perpendicular to the loop plane. The second type has a habit plane near to $\{100\}$ and a displacement vector which is probably perpendicular to the habit plane. Both kinds are interstitial in nature.

In order to determine the Burgers vectors unambiguously by contrast analysis, observation of the same defect for many different low index $\vec{g}$ vectors is necessary. $\langle 100 \rangle$ oriented foils were used in addition to $\langle 111 \rangle$ foils and the selection of different $\vec{g}$ vectors was facilitated by a high angle tilting stage which could be rotated up to 60° in any direction.

A typical example is shown in Fig. 1. Figures 1(a) through (d) were taken near $[001]$ orientation. The foil was then rotated to $[011]$ and $[0\bar{1}1]$, orientation with the diffraction ($\vec{g}$) vectors as indicated [Fig. 1(e) and (f)]. Micrographs taken near $[0\bar{1}1]$ orientation with $[022]$ diffracting vectors were not included in this figure. However, the observed diffraction contrast is tabulated.

A contrast analysis showing contrast observed for different $\vec{g}$ vectors for each of these linear defects is shown in Table 1. For example only a Burgers vector along the $[\bar{1}\bar{1}\bar{1}]$ direction is consistent with all the observed contrast changes for loop A. Other Burgers vectors such as $[001]$ or $[\bar{1}\bar{1}0]$ can not satisfy the observed contrast either in $[011]$ or $[0\bar{1}1]$ orientation. Similarly, only $[11\bar{1}]$ and $[\bar{1}\bar{1}\bar{1}]$ satisfies all observed contrast for loops A and D respectively.

A very weak contrast for defects a and d in $[001]$ orientation for all different diffraction ($\vec{g}$) vectors suggests that the Burgers vector is near to being parallel to the beam direction, e.g., $[001]$. The contrast observed in $[011]$ and $[0\bar{1}1]$ orientations for defect a and d is also consistent with a Burgers vector near $[00\bar{1}]$.

Fig. 1. Diffraction contrast of rod-like defects in different orientations. (a) through (d) are near $\langle 001 \rangle$ orientation. (e) and (f) are near $\langle 011 \rangle$ orientation. (XBB 763-3109)

b. The Shrinkage of Rod-Shaped Defects in Boron Ion-Implanted Silicon

Wei-Kuo Wu

Three different types of rod-shaped defects formed during post-implantation annealing of boron implanted silicon are distinguished in annealing experiments carried out on transmission electron microscope specimens. It is shown that rod-

shaped defects can be boron precipitates, Frank dipoles or perfect $a/2 \langle 110 \rangle$ dipoles. All shrink from the ends only during annealing. The temperature dependence of shrinkage rate for the first type was determined by measuring dl/dt at three different temperatures for a given isolated defect. Boron diffusion appeared to be the rate determining process. The second type, Frank dipoles, were often observed to unfault, transforming into the third type during annealing. At the time of

Table 1. Diffraction contrast of rod-like defects with different g vectors.

Defect No.	$\vec{g}$						$\vec{b}$	$\vec{n}$	Type
	$\hat{n} = [001]$	$\hat{n} = [0\bar{1}1]$	$\hat{n} = [011]$						
	$[220]$	$[2\bar{2}0]$	$[\bar{4}00]$	$[040]$	$[022]$	$[0\bar{2}2]$			
A	O	N	I	O	E-O	R	$[\bar{1}\bar{1}\bar{1}]$	$[111]$	Interstitial
$\bar{A}$	I	N	O	I	R	E-O	$[11\bar{1}]$	$[\bar{1}\bar{1}1]$	Interstitial
D	N	O	I	I	R	E-O	$[\bar{1}\bar{1}\bar{1}]$	$[\bar{1}\bar{1}\bar{1}]$	Interstitial
a	R	N	R	R	O	O	$[00\bar{1}]$	$[001]$	Interstitial
b	E-O	E-O	E-O	R	H-O	N	$\pm[100]$		
c	E-O	E-O	R	E-O	I	I	$\pm[010]$	$\pm[010]$	Interstitial
d	N	R	R	R	O	O	$[001]$	$[001]$	Interstitial
c	E-O	E-O	R	E-O	I	I	$\pm[010]$	$\pm[010]$	Interstitial
f	E-O	E-O	E-O	R	N	H-O	$\pm[100]$		

O Outside contrast
 I Inside contrast
 R Residual contrast; $\vec{g} \cdot \vec{b} = 0$, $\vec{g} \cdot \vec{b} \times \vec{a} \neq 0$
 N No contrast; $\vec{g} \cdot \vec{b} = 0$, $\vec{g} \cdot \vec{b} \times \vec{u} = 0$
 E-O Edge-On
 H-O Head-On

unfaulting the newly formed perfect dipole was always observed to rotate on its glide cylinder to near edge orientation.

The first two types of defects are shown in Figs. 2 and 3. Type a and type A defects are parallel to each other along $\langle 110 \rangle$ but show opposite diffraction contrast (one shows weak outside contrast while the other has strong inside or vice versa). Type a were observed to shrink much faster than type A and completely disappeared by about 900°C. Type A showed irregular shrinkage rates as in Fig. 2(a) and (b), and some were still present up to 1017°C. Also they sometimes showed clear stacking fault fringes [as shown in Fig. 2(e)]. This is consistent with the conclusions of the previous contrast analysis that one kind of linear defect is a faulted Frank dislocation dipole.¹ The widths of type a defects, as evidenced by the diffraction contrast, remained the same as they became progressively shorter in length (Fig. 3). However the widths of type A sometimes increased (Fig. 2). Isolated type a defects shortened in length at a constant rate which depended on the annealing temperature. The temperature dependence of the shrinkage rate for type a defects was found to be 3.5 ± 0.1 eV. This corresponds closely to that for diffusion of boron atoms in silicon but is much too small for silicon self-diffusion under equilibrium conditions.

Transformation of a type A defect is shown in Fig. 3. The defect, A, suddenly changed into

a perfect dislocation loop which rotated into a $\langle 112 \rangle$ direction with its new Burgers vector perpendicular to its new elongated direction.

The irregular and generally slower shrinkage rate for type A, rod-shaped defects, such as A in Fig. 2 made apparent activation energy measurement impossible in this temperature range. However, from the stacking fault fringe contrast as shown in Fig. 2(e) and from their frequent sudden transformation over their entire length to perfect dislocation dipoles that rotated on their glide cylinders to a $\langle 112 \rangle$ orientation it was concluded that this type of defect was primarily formed from interstitial silicon atoms and that it was essentially a Frank dislocation dipole.

It is possible that all rod-shaped defects are initially thin boron precipitates but that during the early stages of growth some transform into faulted dipoles because they are nucleated in or grow into a region of high silicon interstitial concentration.

c. Climb of Dislocations in Boron Ion-Implanted Silicon

Wei-Kuo Wu

The only observable defects that remain in boron ion-implanted silicon (2×10^{14} ions/cm²)

Fig. 2. Isochronal annealing sequence of rod-shaped defects of type a and type A in boron ion implanted silicon. Picture (a) was bulk annealed at 800°C for 20 minutes before thinning. Figures (b) through (e) were taken after thin foil annealing at 850°C, 900°C, 952°C, and 1017°C for 20 minutes respectively. (XBB 765-4223)

after heating to about 1000°C are a few faulted interstitial loops of burgers vector $1/3 \langle 111 \rangle$ and some perfect loops, burgers vector $1/2 \langle 111 \rangle$. We have studied the shrinkage of these loops in the temperature range near 1000°C where the most likely diffusion mechanism in silicon is formation and migration of self-interstitial atoms.

Figure 4 shows a typical annealing sequence which was obtained by repeatedly removing the specimen from the electron microscope and annealing it at constant temperature in a furnace for a measured time. After each annealing treatment the same area was located and rephotographed. By measuring the shrinkage rate of several such loops at a given temperature and then measuring the shrinkage rate of the same loops at slightly higher or lower temperature an accurate determination of the activation energy for silicon self-diffusion can be made provided that the shrinkage rate is diffusion controlled rather than emission controlled. A value of 5.5 eV was determined from measurements of loops in the series shown in Fig. 4 and also from other similar series made on elongated perfect loops.

Two features of the series in Fig. 4 are consistent with the assumption that shrinkage rate is diffusion controlled: First, the shrinking loops adopt almost perfectly circular shapes (see loops B and C which are lying in the plane of the foil and are therefore projected in true shape). This indicates that jog formation at the corners of a hexagonal loop is not the

rate determining step. Second, the pair of loops, A, when they join quickly assume an elliptical shape because the concave part becomes a sink for the interstitial atoms that are emitted at the outer ends; this sink is located at a short diffusion distance. The diffraction contrast indicates that all of the loops are located close to one surface of the foil. However, the surface is a relatively poor sink for interstitials as can be seen by the slow shrinkage rate of loop F which is actually cut by the surface. The reason for this is most likely the existence of slightly oxidizing atmospheres during all the annealing treatments. From 1 to 2 oxidation was more severe than during the rest of the series and it can be seen that all the larger loops actually grew, assuming hexagonal shapes. The driving force for shrinkage of a Frank loop is the stacking fault plus the line tension. The latter only begins to make a significant contribution for loops smaller than loop H. These smaller loops shrink at an accelerating rate; in this case probably by diffusion of interstitials to the nearest larger loops.

d. Model for the Development of Secondary Defects in Phosphorous Ion-Implanted Silicon

K. Seshan

When ions are implanted into silicon in order to dope it, it has been experimentally shown that

Fig. 3. Similar annealing sequence as in Fig. 2. Note that type a rod-shaped defect suddenly changes into an elongated perfect dislocation loop and rotates into $\langle 112 \rangle$ orientation. The dotted line shows its previous position. (XBB 765-4224)

for doses below D_c (critical dose for formation of a continuous "amorphous" layer) where the "amorphous" zones if any, do not overlap, secondary interstitial dislocation loops large enough to be studied by transmission electron microscopy are formed when the specimen is heated to 800°C , see Fig. 5.

A three-stage model to explain the development of such secondary interstitial defects in ion-implanted silicon has been developed. The model requires that in addition to vacancy clusters small interstitial clusters exist between room temperature implantation and about 750°C and that these clusters release mobile interstitial silicon and dopant atoms above 750°C .

For doses above D_c where a continuous buried amorphous layer is formed, a layer of complex faulting is formed in addition to a layer of interstitial loops which lie at a greater depth below the implanted surface.

It is proposed that the observed defect distribution can best be explained by the outward growth of small crystalline regions inside the "amorphous" region, Fig. 6. This is in contrast

to the accepted view that regrowth occurs by migration of two slightly misaligned lower and upper growth surfaces which meet to produce the faulted layer.

e. Characterization of Secondary Defects in Silicon Implanted with Phosphorous Ions to a Dose that Produces a Continuous Buried Amorphous Layer

K. Seshan

Wafers of 111 silicon, p-type, were implanted with 100 keV P^+ ions to a dose (3×10^{15} ions/ cm^2) where the primary damage produces a buried, continuous "amorphous" layer. The secondary defects formed upon annealing were examined using the weak-beam electron microscopy technique. A heavily faulted layer at a depth of about 0.1μ was observed, see Fig. 7. Below this is a layer of dislocation loops, and even stacking fault tetrahedra at a depth of about 0.5μ . The tetrahedra are believed to be of vacancy type, this being the first report of their presence in ion-implanted silicon.

Fig. 4. Shrinkage of interstitial Frank loops in silicon due to high temperature dislocation climb. (XBB 7611-10015)

Fig. 5. Simple secondary defects formed when ion-dose is below D_c . Contrast this with the complex defects formed above D_c . (Mag. 270 K).

(XBB 760-11120, left)

The heavily faulted region contains a variety of planar defects including double single and interconnected stacking faults, micro-twins and dislocations. Characterization of the stacking faults and multiple stacking faults is difficult as the faults are completely within the buried

Fig. 6. Proposed model for the as implanted state to explain the observed secondary defects when dose is above D_c . The small crystalline areas decrease in diameter with increase of ion dose.

(XBB 760-11120, right)

damaged layer. A few in the thinnest areas which cut the foil surface show precipitate and π -boundary type contrast, indicating possible dopant atom adsorption on the stacking fault.

The formation of clusters of faults and dislocations is explained assuming outward growth from small crystalline nuclei within the so-called buried "amorphous" layer.

Fig. 7. Weak-beam dark-field image of the heavily faulted layer showing the complex arrangements of twins and stacking faults. Insert shows a fault on 3 planes and the π -boundary type fringes (top left). (XBB 760-1119)

3. RESEARCH RELATED TO UTILIZATION OF SOLAR ENERGY

a. Preparation of $\text{Cd}_{1-y}\text{Zn}_y\text{S}$ Films for Study of $\text{Cd}_{1-y}\text{Zn}_y\text{S}/\text{Cu}_x\text{S}$ Heterojunction Photovoltaic Cells

Barry Chin

$\text{Cd}_{1-y}\text{Zn}_y\text{S}$ single crystal films are being grown for study of heterojunction photovoltaic cells. The hot-wall vacuum deposition technique has been adapted for the heteroepitaxial growth of the mixed crystal $\text{Cd}_{1-y}\text{Zn}_y\text{S}$ onto (111) single crystal GaAs substrates. The proposed experimental heterojunction photovoltaic cell will be a back wall configuration with the Cu_xS layer protected from the environment by the mixed crystal film.

A two-source hot wall evaporator has been constructed to allow for the simultaneous evaporation of CdS and ZnS sintered grains (see Fig. 1). A baffle has been placed between the two sources to reduce the effects of the high Zn partial pressure over the cadmium sulfide source. A second baffle is situated between the sources and substrate to reduce radiative heating from the crucibles to the substrate.

The (111) GaAs substrates are etched in 2%Br:CH₃OH solution for five minutes to remove any oxide film before deposition. The substrate holder assembly is rotated away from the cylinder and is outgassed along with the cylinder to a temperature of $\sim 600^\circ\text{C}$. When the pressure in the vacuum system decreases to below 1×10^{-5} Torr, the substrate heater assembly is rotated into position above the sources so that a tight seal is formed to the cylinder. The power to the substrate heater is turned off and the temperature of the holder is allowed to decrease. The power used to heat the two sources is then set and monitored throughout the deposition run.

Fig. 1. Two source hot wall vapor deposition apparatus. (XBL 773-5191)

The deposition rate is varied by adjustment of the power delivered to the sources and the temperature of the cylinder and substrate. Since the temperature of the two sources also determines the composition of the film, the thickness may be varied by the time duration of the deposition. X-ray analysis, x-ray microprobe, energy dispersive analysis of x-rays (EDAX), and scanning electron microscopy are used to determine the composition, crystallinity, thickness, and surface morphology of the deposited films.

Table 1 gives some mixed crystal film results. It was observed that thicker films were grown by surface diffusion on the "back" of the exposed (111) As face substrate. To understand this result a deposition was conducted with two substrates: a polished (111) As face and an unpolished (111) Ga face exposed to the sources. Film growth on the Ga face was found to be greater. This may be explained by the higher sticking coefficient of Zn and Cd to the Ga face in forming the first monolayer than the sticking coefficient of S to the As face.

Nonuniform composition profiles through the thickness of the film (were observed). SEM-EDAX scans showed a decrease in Cd concentration and a simultaneous increase in Zn concentration during the deposition which was probably due to formation of a ZnS layer directly on the CdS source material. These "poisoned" CdS charges with the ZnS outer layer were then used in subsequent deposition runs. These have been found to produce films with a more uniform composition.

Another difficulty in mixed crystal film growth has been the formation of misoriented grains. Single mixed crystal films are desired for comparison with previous results obtained on single crystal photovoltaic cells. The x-ray diffractometer scans in Table 1 gave peaks

Table 1.

Run	ZnS current (amps)	CdS current (amps)	Deposition time (minutes)	Substrate temp. (°C)	Cylinder temp. (°C)	Crystallinity s = single p = poly	Thick- ness (μm)	Composition y in Cd _{1-y} Zn _y S for (hkl)
1	46	30	60	495	600	p	30	(002) y = 0.15, 0.86 (103) y = 0.26 (004) y = 0.22
2	46	25	60	480	600	p	30	(002) y = 0.10 (002) ZnS (102) y = 0.08 (103) y = 0.10
3	43	25	60	485	600			Non-uniform
4	41	23	60	470	600	p	~24	(002) y = 0.13 (102) y = 0.20 (103) y = 0.15 (104) y = 0.10
5	37	20	90	460	600	p	7	(002) ZnS (102) y = 0.31 (103) y = 0.29
6	37	20	90	420	550	s	~2	(002) ZnS
7	39	23	90	420	550	s	~3	(002) y = 0.70 Broad x-ray peak
8	39	24	180	430	560	p	~11	(002) y = 0.8 (102) y = 0.28 (103) y = 0.29
9	39	24	110	430	560	p	10	(002)CdS (101)y = 0.10 (102) y = 0.13 (103)y = 0.1
					As face Ga face unpol.	p	10-45	(002) y = 0.10 (102)y = 0.1 (103) y = 0.15 (104)y = 0.1
10 Ga face pol.	39	24	110	430	560	p	12-20	(102) y = 0.10 (103) y = 0.11
11 Ga face pol.	37	22	180	420	560	"s"	<1-13	(002) y = 0.15 (002) y = 0.75
12 Ga face pol.	37	22	180	395	560		<1	second baffle used
13 Ga face Unpol.	38	22	180	450	600	s	<1	(101) y = 0.25 (202) y = 0.19

corresponding to (102), (103) and (104) reflections for many of the polycrystalline films. This indicates that the misorientation of the c-axis from the normal to film growth is less than 20°. To prevent polycrystalline growth lower deposition rates and longer growth runs have been implemented.

b. On the Potential Advantages of the Mixed Crystal Cd_yZn_{1-y}Cu_xS Solar Cell Compared to the Conventional CdS-Cu_xS Cell

Terry Peterson

Having shown that there are important advantages in substituting a "mixed" crystal of (Cd, Zn)S

for the CdS layer in a Cu_xS -CdS heterojunction photovoltaic energy converter (LBL-3985), we have proceeded on a program to further investigate the properties of the new "mixed crystal cell." The aim of this program is to establish the behavior of this kind of structure as a function of the cadmium-to-zinc ratio in the mixed crystal. It was hoped that this structure would exhibit electrical effects due to the changing lattice mismatch between the Cu_xS and different mixed crystal compositions. However, it now appears, because of recent results elsewhere on CdS cells, that the electrical characteristics of the mixed crystal cell are dominated by the decrease in electron affinity accompanying an increase in zinc content of the mixed crystal. Nevertheless, the mixed crystal cell should still represent a substantial improvement over CdS cells for solar-energy conversion. Of equal importance, it should also be a valuable tool for improving the understanding of heterojunction devices in general.

c. Design of a Test Collector for Comparison of Spectrally Selective Surface Coatings for Efficient Collection of Solar Energy

Carl Lampert

Our solar test collector was designed to make practical quantitative comparisons between various absorbing surfaces without the use of elaborate and costly equipment. The design consists of a collector fed by a controlled temperature bath which supplies an inlet fluid at a selected temperature in the range from 25°C to 90°C (77°F to 194°F). This temperature is maintained by a custom electronic controller. A small variable flow pump circulates water through three collector pipes at a selected flow rate. The collector pipes consist of some type of metallic material (e.g., steel or copper) covered by a selective (e.g., black chrome, black nickel) or non-selective coating (such as black paint). The collector body is designed in such a way that it permits easy removal and replacement of the test pipes. Under the outer two pipes heating strips have been placed to compensate the edge losses of the outer pipes and thus simulate a large scale collector for the center pipe. This is achieved by a differential temperature controller which maintains constant temperatures on all the pipe outlets. Across the central test pipe both inlet and outlet temperatures are recorded within about one degree accuracy. The collector body may be set at any desired tilt angle to the sun to suit the season. Simultaneous measurements of solar radiation and wind direction and velocity are also made.

This design allows different types of selective and non-selective surfaces to be tested and evaluated in terms of collection efficiency at various operating temperatures. Currently, the collector is being used to evaluate black chrome and painted surfaces for solar energy collection.

4. MICROSTRUCTURAL STUDIES OF ASBESTOS AND RELATED MINERALS

K. Seshan and H.-R. Wenk*

Interest in asbestiform minerals stems from the fact that they are carcinogenic¹ and that they occur abundantly in the California air and water. California is the leading producer of asbestos in the U.S.¹

It was reported earlier^{2,3} that faulting and twinning at a microscopic scale may be responsible for the asbestiform (finely fibrous) morphology that is often exhibited by these minerals. (See Figs. 1 and 2). In order to verify this hypothesis we are studying naturally occurring asbestiform minerals found in California CHOCIDOLITE (Fig. 1) and TREMOLITE (samples from Professor Wenk's mineral collection). A great variety of microstructures has been encountered, most of which are hitherto unreported, twist boundaries and rotation boundaries, small angle grain boundaries, stacking faults twins and morphology varying from rotated crystallites to very fine (20 nm) (200Å) needles, (see Fig. 2 for example). The minerals have been found to be surprisingly stable in the electron beam. We are in the process of characterizing the crystallography and various morphologies. A possible explanation for the asbestiform morphology is under study.⁴

In related work the microstructure of the mineral plagioclase, the most abundant rock forming mineral from the San Andreas Fault zone, is being studied (Fig. 3). Optical micrographs show that extensive twinning and faulting has occurred. This is in contrast to feldspars from other geographical areas which are largely undeformed.

We plan to characterize such faults and hope by this to obtain additional insight into the basic processes involved in the tectonic deformation which is responsible for this microstructure.

* Dept. of Geology and Geophysics, University of California.

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Fig. 1. Optical micrograph of the needle like morphology of crocidolite. (Mag. x90)

Fig. 2. Electron micrograph of the same mineral as in Fig. 1. Notice the fine needles no more than 200Å (Mag. 90 K)

Fig. 3. Optical micrograph of Plagioclase from the San Andreas Fault zone showing the fine distribution of microtwins. (Mag. x90)
(XBB 760-11121)

5. RESEARCH PLANS FOR CALENDAR YEAR 1977

Jack Washburn

Continuation of the work on the mechanism of dislocation climb and swelling of metals during high temperature radiation damage will include further measurements of relative climb rates of edge and near-screw dislocations, in copper, a study of "subthreshold" production of free interstitials and vacancies in aluminum and measurements of swelling rates of "low-swelling" alloys to very high fluence (500 dpa). All of this work is related to a more complete understanding of the behavior of materials in the high temperature radiation environments that exist in nuclear power plant cores.

The work on semiconductors will emphasize ion-implantation damage in silicon. It will include further work on the regrowth of "amorphous" layers with the aim of better understanding the structure of the "amorphous" layer and the origin of the stacking faults, micro-twins, dislocation networks and vacancy tetrahedra that have been observed after regrowth.

The program on mixed crystal $Zn_yCd_{1-y}S-Cu_xS$ solar cells will emphasize the preparation of

good single crystal mixed crystal layers by epitaxial growth on GaAs. The long range aim of the program is to be able to make comparisons of the properties of mixed crystal and conventional CdS- Cu_xS heterojunctions without the complication due to the presence of grain boundaries. This research is complementary to programs aimed at development of low cost solar cells.

Further work on development of low cost spectrally selective coatings for efficient collection of solar heat will concentrate on better characterization of the successful "black chrome" coating. Further transmission electron microscopy and electron diffraction studies are needed to determine the size range of Cr particles and the thickness of chromium oxide that are present in this complex electrodeposit.

A cooperative program with Professor Wenk of the Geology Department on growth and deformation defects in naturally occurring minerals will be continued. Relatively little transmission electron microscopy has been done in this area. This work could lead to better understanding of the conditions that have existed in the earth's crust during the times when rock deformation took place and may also lead to more reliable methods for identifying potentially harmful fibrous mineral pollution of air and water.

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3. PHYSICAL PROPERTIES

a. High Field Superconductivity

Milton R. Pickus, Principal Investigator

Introduction. The infiltration process developed at MMRD has been applied to the niobium-tin system to produce multifilamentary tape and wire with excellent high field current-carrying capacity. During the past year, research was conducted to more fully characterize the niobium-tin conductors, and to assess the versatility of the process by applying it to other systems whose A15 phases have higher values of the critical temperature and critical field than those of Nb_3Sn . The ternary Nb-Al-Ge system was selected to initiate work on this aspect. Despite much effort on this system in other laboratories, involving different approaches, there has been no reported success in producing a multifilamentary conductor based on the A15 compound, $\text{Nb}_3(\text{Al},\text{Ge})$. The results summarized in this report demonstrate that this has been accomplished by means of the infiltration process.

1. STUDIES OF FILAMENTARY Nb_3Sn WIRES MADE BY THE INFILTRATION PROCESS

Kanithi Hemachalam and Milton R. Pickus

The fabrication involves achieving a controlled porosity in sintered niobium, infiltrating the pores with molten tin and mechanically reducing the composite to a fine wire. The Nb_3Sn filaments, typically 1-5 μm in size, are formed by a short heat treatment at a temperature of 950°C. In Fig. 1, the critical current density of the

Fig. 1. Critical current density of the Nb_3Sn -Nb core as a function of magnetic field for pulsed and steady field conditions. (XBL 7512-9472A)

Nb_3Sn -Nb core is shown as a function of magnetic field for both pulsed and steady field conditions. The critical temperature has been found to be nearly constant at 17.9°K for reactions carried out at temperatures between 930° and 1200°C, and to decrease when the reaction temperature is lower than 930°C. In contrast, the critical current density vs. magnetic field characteristics deteriorate rapidly when the heat treatment is performed at temperatures above 1000°C. This behavior is shown in Fig. 2. The times required for a complete

Fig. 2. Current density of 0.3 mm diameter core at 50, 100 and 150 kG as a function of reaction temperature. (XBL 7512-9471)

reaction of the tin with the niobium matrix at 700°, 800° and 900°C were 50 hours, 2 hours and 0.5 hours respectively. Between 950° and 1000°C, a reaction time of only 2 minutes is sufficient. Increasing the reaction period at 950°C up to 30 times the minimum required for a complete reaction had no adverse effect on the critical current density.

The decrease in critical current resulting from bending the wires was evaluated by wrapping 15 cm long sections around a mandrel, straightening them and remeasuring the critical current. The same samples were bent around successively smaller mandrels. The critical current $I_C(D)$ for a bend diameter D , normalized to the critical current prior to bending, $I_C(\infty)$, is shown in Fig. 3 for two specimens. The minimum diameter to which the wires can be bent with no degradation in critical

Fig. 3. Degradation of current-carrying capacity with bending diameter for two wires.
(XBL 7510-7538B)

current is 2 cm. Another desirable characteristic of multifilamentary niobium-tin wire made by the infiltration process was determined. The rate at which the critical current density decreases with increasing field is significantly less for this type of wire than that for wires made by other processes.

2. MULTIFILAMENTARY Nb-Nb₃(Al,Ge) SUPERCONDUCTORS

Milton R. Pickus, Moshe P. Dariel, John T. Holthuis, John Ling-Fai Wang and José Granda

The infiltration process used successfully for the niobium-tin system has been adapted for application to the ternary Nb-Al-Ge system. This research has resulted in the first reported multifilamentary superconductor based on Nb₃(Al,Ge). The special significance of this achievement lies in the fact that this A15 compound has the highest critical temperature and critical field of any known material, with the exception of the metastable compound Nb₃Ge. The latter compound has been prepared only in the form of thin films by such methods as sputtering and chemical vapor deposition.

The process involves preparation of a porous niobium matrix by powder metallurgical techniques. The pores are then infiltrated with a liquid Al-Ge alloy having the eutectic composition. Figure 1 shows the microstructure after infiltration. Elongation of the composite by appropriate mechanical deformation, such as form rolling, produces multiple connected Al-Ge filaments aligned within the niobium matrix in the deformation direction. These filaments are converted to the superconducting A15 compound by a heat treatment that causes a diffusion reaction between the Al-Ge eutectic and the niobium matrix. The resulting microstructure is shown in Fig. 2.

Fig. 1. Sintered Nb compact infiltrated with an Al-Ge eutectic alloy.
(XBB 768-6629)

Fig. 2. Scanning electron micrograph of Nb₃(Al,Ge) filaments in a Nb matrix.
(XBB 768-6630)

In this preliminary study, critical temperatures and critical current densities were measured for samples diffusion-reacted in the temperature range of 1250 to 1700°C. The superconducting properties were found to depend not only on the time and temperature of the diffusion reaction, but also on the duration of a post-reaction anneal at 750°C. The highest critical temperature obtained thus far is 19°K. A critical current density of 10^5 A/cm² was observed at 50 kOe. This represents about a tenfold improvement over published data for bulk conductors based on the Nb-Al-Ge system, as shown in Fig. 3. We can expect that further optimization of the processing parameters will lead to improved properties with respect to both the current-carrying capacity and the critical temperatures.

Fig. 3. Magnetic field dependence of the critical current density for Nb₃(Al,Ge) bulk superconductors. (XBL 767-3192A)

3. KINETIC STUDIES OF POROUS NIOBIUM INFILTRATED WITH THE Al-Ge EUTECTIC COMPOSITION

E. Kannatey-Asibu Jr., John Ling-Fai Wang and Milton R. Pickus

This study was undertaken to generate basic kinetic data required for optimizing the superconducting properties of the multifilamentary Nb-Nb₃(Al,Ge) conductors recently developed in this laboratory. Of particular interest is the influence of time and temperature on the growth and grain size of the Al₁₅ phase.

Figure 1 shows a typical scanning electron micrograph of an infiltrated sample after reaction. By using special etching techniques, the width and grain size of the Al₁₅ phase are clearly delineated.

Fig. 1. Scanning electron micrograph of infiltrated and reacted sample showing width and grain size of Al₁₅ phase. (1) Ge-rich phase; (2) Al₁₅; (3) Nb matrix. (XBB 760-11000)

From measurements of these parameters over a range of temperatures and times their variation with heat treating schedules has been determined, as shown in Figs. 2 and 3. Work in progress will extend the temperature range investigated down to 1300°C.

Information on growth rate is essential for controlling the diffusion reaction by which the Al₁₅ phase is formed. Grain boundaries are known to be effective flux pinning sites. Therefore, the grain size must be restricted to favor high current-carrying capacity.

Fig. 2. Influence of time and temperature on width of Al₁₅ phase. (XBL 7612-4499)

Fig. 3. Influence of time and temperature on grain size of Al5 phase. (XBL 7612-4498)

4. A QUENCH-AGE METHOD FOR THE FABRICATION OF Nb-Al SUPERCONDUCTORS

Robert L. Ciardella, Moshe P. Dariel, John Ling-Fai Wang and Milton R. Pickus

A composite Nb-Nb₃Al superconductor, prepared by taking advantage of the extended, high temperature solid solubility of Al in Nb, is shown in Fig. 1.

Fig. 1. Central core of the Al5 phase embedded in the Nb matrix. The dark interfacial areas have a composition corresponding to the two phase, Nb(Al) and Nb₃Al, region of the Nb-Al phase diagram. (XBB 7511-8540)

Rapid quenching after an elevated temperature (1950°C) solution treatment makes it possible to retain at room temperature a metastable solid solution containing more than 20 at.% Al. The solid solution transforms into the Al5 phase in the course of a short and relatively low temperature (850-1000°C) aging treatment. The formation of the Al5 phase at temperatures below 1000°C is highly significant. Other investigators have shown that it was not possible to form the Nb₃Al compound

by means of a diffusion reaction at temperatures below 1100°C even by starting with an extremely fine distribution (300 Å) of the reaction components.

Metallographic studies have shown that mechanical twinning is an important mode of deformation of both the stable and metastable solid solution. It has been found that in the course of the aging treatment the metastable solid solution can transform into the Al5 phase by two mechanisms. At high aging temperatures the morphological features observed are characteristic of a massive transformation. For lower aging temperatures and for Al concentrations up to the maximum retainable, precipitation of the Al5 phase occurs preferentially along grain boundaries and the twin network. By a judicious choice of conditions, it is possible to prepare a sample in which the Al5 phase forms almost exclusively along the twin network, as shown in Fig. 2. In principle, therefore, a multifilamentary Al5 configuration can be achieved in this manner.

Fig. 2. Al5 precipitates along the twin network, formed in the course of the aging treatment. (XBB 7511-8537)

5. RESEARCH PLANS FOR CALENDAR YEAR 1977

Milton R. Pickus

Now that we have shown that multifilamentary conductors based on the compound Nb₃(Al,Ge) can be produced by the infiltration process, our next priority is to elucidate the kinetics of the system. This is necessary to optimize the superconducting properties. At the present time, we find that the best values of the critical temperature are obtained by using high reaction temperatures (1600-1700°C), whereas the critical current density is markedly improved by decreasing the temperature of the reaction anneal (~1300°C), and its duration. We will investigate several approaches for controlling the grain size of the Al5 phase -- an important parameter with respect to current-carrying capacity. Also, we will investigate ways of minimizing deviations from stoichiometry. In this connection, we will try to exploit an observation made during the past year. We have found that at temperatures as low as 400°C,

the aluminum-germanium eutectic reacts with some of the niobium matrix to form a single phase material, which is a niobium lean compound, $\text{Nb}(\text{Al},\text{Ge})_3$. This should provide a simpler diffusion system that is easier to control.

We also plan to pursue another observation we made. The Al-Si eutectic appears to be much more ductile than the Al-Ge eutectic. In fact, a literature survey made since has disclosed evidence that the silicon eutectic exhibits weak superplasticity, and that at lower silicon contents the superplastic effect becomes much stronger. This should greatly facilitate the necessary deformation of the niobium composites. Furthermore, there have been theoretical predictions that the Al_5 compound, Nb_3Si , should have a critical temperature in the neighborhood of 35°K . For these reasons, we will attempt the preparation of multifilamentary conductors based on the Nb-Al-Si system.

Our recently completed powder making facility has the capability of providing a rapid quench from the liquid state. We plan to investigate the potential of this equipment for the preparation of high T_c , metastable Al_5 compounds, such as Nb_3Ge .

Some basic research on a scale-up of the infiltration process is also planned. Its objective would be the preparation of sufficiently long lengths of wire or tape so that performance tests on coils could be carried out.

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b. Microstructure and Mechanical Behavior of Ceramics; Glass- and Ceramic-Metal Systems

Joseph A. Pask, Principal Investigator

Introduction. A major objective of the research program deals with correlations of character (with emphasis on microstructures and nature of grain boundaries) with mechanical behavior and corrosion resistance at high temperatures, and with determining the factors that play a role in obtaining a ceramic material with a designed character. It involves studies on the mechanisms responsible for the mechanical behavior of single crystals, and on the application of such knowledge to the understanding of the behavior of polycrystalline ceramic materials. It also involves studies on the kinetics and mechanisms of solid-state reactions, sintering, and distribution of phases in a multiphase system.

The compositions under study--mullite, alumina, fosterite, spinel, magnesia--are basic materials of industrial ceramics and refractories, and sintering is the basic method for their manufacture. The fundamental approach in these studies in terms of physical chemistry, solid-state chemistry, and dislocation theory also makes the work relevant in that the determined principles should be applicable to other polycrystalline metal, ceramic, and composite materials.

A second objective of this program is concerned with structural, thermodynamic, and electrochemical studies of glass-metal and ceramic-metal systems. It involves studies related to wetting, bonding, and the nature of the interfaces between dissimilar phases; to the thermodynamics and kinetics of chemical reactions at such interfaces; and to the kinetics and mechanisms of dissolution and diffusion in glasses. A basic understanding of the nature of interfaces and the mechanisms of reactions at interfaces is critical in all materials.

1. EXPERIMENTS ON MULLITE PHASE EQUILIBRIA

Victor F. Draper and Joseph A. Pask

It was definitely established that two types of mullite (nominal composition of $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) existed: a stable 3:2 type that formed by chemical interdiffusion at temperature, and a metastable 2:1 type that formed by precipitation from aluminum silicate melts on cooling. The solid solution range of stable mullite as shown in Fig. 1 was established by the diffusion couple technique.¹ A series of aluminum silicate melts with Al_2O_3 content ranging from 65 to 87.5 wt% after homogenizing at 2156°C for 15 minutes, quenching to 1804°C , holding for 12 hr, and then quenching to room temperature had precipitated metastable mullite with increasing Al_2O_3 content as the Al_2O_3 content of the mixture increased up to ~82 wt% with no precipitation of $\alpha\text{-Al}_2\text{O}_3$. Melts with higher Al_2O_3 contents showed precipitates of $\alpha\text{-Al}_2\text{O}_3$ and mullite with lower Al_2O_3 contents. These data support the predicted

Fig. 1. $\text{Si}_2\text{-Al}_2\text{O}_3$ system showing the stable and metastable phases as determined by Aksay and Pask.¹ (XBL 755-1377A)

Fig. 2. $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system showing the determined boundary line between the mullite and $\alpha\text{-Al}_2\text{O}_3$ primary phase fields and isotherms for the mullite and estimated isotherms for the corundum, calcium hexaluminate and calcium dialuminate phase fields. (XBL 764-1632C)

metastable phase diagram for SiO_2 - 2:1 type mullite shown in Fig. 1.

Melts with $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratios corresponding to 3:2 mullite with CaO additions up to 10 wt% exposed to similar heating cycles resulted in precipitated metastable mullite with less than 1 wt% of CaO and Al_2O_3 content up to 83 wt% in solid solution; at higher CaO contents $\alpha\text{-Al}_2\text{O}_3$ was the crystalline phase. Slowly cooled specimens showed similar solubilities. An analysis of controlled experiments indicated the position of the boundary line between the mullite and Al_2O_3 primary phase fields under stable conditions to be as shown in Fig. 2. This corresponds with the peritectic point shown in Fig. 1.

1. I. A. Aksay and J. A. Pask, J. Amer. Cer. Soc. 54 (11-12), 507 (1975).

2. MULLITE CRYSTALLIZATION FROM SiO_2 - Al_2O_3 MELTS WITH EXCESS SiO_2

Subhash H. Risbud and Joseph A. Pask

Aluminum-silicate melts containing 42 and 60 wt% Al_2O_3 were homogenized at 2090°C ($\pm 10^\circ\text{C}$) and crystallized by quenching and various heat treatment schedules in sealed molybdenum crucibles. Under stable equilibrium cooling of the 60 wt% Al_2O_3 melt Al_2O_3 would precipitate

at $\sim 1900^\circ\text{C}$ which would undergo a peritectic reaction with the liquid to form stable (3:2 type) mullite at 1828°C ; under metastable equilibrium cooling metastable (2:1 type) mullite would precipitate at $\sim 1840^\circ\text{C}$ (see Fig. 1 in preceding article No. 1). It was found that strong supercooling existed and that, regardless of heating schedules at temperatures above $\sim 1325^\circ\text{C}$, mullite precipitated only on cooling below 1325°C which is the boundary of the calculated liquid miscibility gap at 60 wt% Al_2O_3 (Ref. 1 and presented in the 1975 Annual Report). The initial-precipitated metastable mullite had ~ 78 wt% Al_2O_3 . Subsequent reheating and soaking resulted in a decrease of the Al_2O_3 content and a corresponding increase of Al_2O_3 content of the glass. The lowest Al_2O_3 content obtained in mullite was ~ 73.5 wt% in melts that were reheated for 110 hr at 1725°C . Figure 1 also shows that growth of mullite crystals occurs with heat treatment.

A spinodal structure was exhibited by a quenched 42 wt% Al_2O_3 melt. This composition on cooling drops into the spinodal region of the miscibility gap at $\sim 1550^\circ\text{C}$. The structure is indicated in the quenched specimen in Fig. 2; the figure also shows growth of mullite crystals with time by a solution-precipitation process.

1. Subhash H. Risbud, Metastability and Crystallization Studies in the Silica-Alumina System, (Ph.D. thesis), LBL-5453, August 1976.

Fig. 1. Growth of mullite crystals with heat treatment at 1725°C in 60 wt% Al_2O_3 melts nucleated by quenching from the homogenizing temperature of 2090°C to room temperature. (XBB 766-5216)

Fig. 2. Growth of mullite crystals with heat treatment at 1725°C in 42 wt% Al_2O_3 melts nucleated by quenching from the homogenizing temperature of 2090°C to room temperature; photo of quenched specimen at left shows spinodal structure. (XBB 766-5225)

3. STRUCTURE, STRENGTH, AND CORROSIVE RESISTANCE OF ALUMINUM SILICATE MATERIALS*

Philip C. Dokko, Robert B. Langston, Michael D. Sacks and Joseph A. Pask

Alumino-silicate refractories are attractive possibilities for use as components in furnaces used for coal gasification processes because of the abundance of the necessary raw fireclay materials. Behavioral characteristics of importance in such applications are resistance to erosion and corrosion. Strength at high temperatures is critical in the development of erosion resistance. Resistance to chemical attack by H_2 in the presence or absence of H_2O vapor is critical in the development of corrosion resistance.

Mullite (72 wt% Al_2O_3) was found to have exceptionally high strength and creep resistance at temperatures up to $1500^\circ C$. Polycrystalline mullite free of glass and theoretically dense (Specimen A in Fig. 1) at $1400^\circ C$ fractures at a

Fig. 1. Stress-strain curves for an applied strain rate of $1 \times 10^{-5} \text{ sec}^{-1}$ at (a) $1400^\circ C$, and (b) $1500^\circ C$. (Specimen A alkoxy-derived polycrystalline mullite free of glass, grain size $2.7 \mu m$; specimen B, grain-size $3.5 \mu m$; Specimen C, grain size $4.2 \mu m$; Specimen F, reactively hot pressed polycrystalline mullite with a glassy phase.) (XBL 766-9003)

stress of $\sim 115,000 \text{ psi}$ at a strain rate of 10^{-5} sec^{-1} and at $1500^\circ C$ at a stress of $\sim 65,000 \text{ psi}$, and exhibited a steady-state creep rate of $\sim 10^{-7}$ at a stress of $\sim 20,000 \text{ psi}$ with a stress exponent of 1 (Specimen A in Fig. 2). Polycrystalline mullite with some glass (Specimen F in Fig. 1) at $1400^\circ C$ showed 10% plastic strain at a stress of $\sim 25,000 \text{ psi}$, and exhibited a steady-state creep rate of $\sim 10^{-5}$ at a stress of $\sim 20,000 \text{ psi}$ with a stress exponent of 1.8 (Specimen F in Fig. 2). Single crystal mullite (nominal composition equivalent to $2Al_2O_3 \cdot SiO_2$ as grown) showed no plastic deformation or failure at $1500^\circ C$ up to $127,000 \text{ psi}$ which was the limit for the testing apparatus, and no creep at $1400^\circ C$ under a stress of $70,000 \text{ psi}$ for 200 hr. The indications are that dislocations, if present, are not mobile under the testing conditions. This

Fig. 2. Steady-state creep rate vs. stress at $1400^\circ C$. (Specimen D, hot pressed). (XBL 766-9002)

inherent strength of mullite has not been fully realized in commercial materials containing mullite because of the presence of a glass which becomes a liquid at high temperatures. Even in the absence of a recognizable glassy phase, the presence of grain boundaries reduces the strength in comparison with a single crystal of mullite.

Seven commercial refractories (ranging in Al_2O_3 content from 43 to 85 wt%) were obtained for an exploratory analysis of strength and corrosion resistance. In all cases a microstructure analysis indicated considerable nonhomogeneity with presence of porosity and a glassy phase. The importance of microstructure is indicated by the fact that even at $1200^\circ C$ the highest ultimate stress realized was $\sim 11,000 \text{ psi}$ in comparison with the high strengths of the laboratory-prepared specimens. After heat treating all of the specimens at $1700^\circ C$ the highest stress of $\sim 13,000 \text{ psi}$ at $1200^\circ C$ was exhibited by the specimen with 47 wt% Al_2O_3 and not the one with 85 wt%. Microstructure examinations indicated that this was due to greater homogeneity and the formation of a mullite framework structure in the strong specimen.

While the H₂ furnace was in the process of construction and evaluation, resistance to attack by 15% HF aqueous solutions after exposure for 24 hr at room temperature was determined. The dense polycrystalline mullite specimen showed essentially no loss in weight while the commercial specimens showed losses ranging from 5 to 35 wt% and from 4 to 28 wt% after heat treatment at 1700°C. The weight loss increase was correlated with the increase in SiO₂ content which was related to an increase of glass content in the refractories. The removal of the glassy phase also resulted in a decrease of strength in comparison with the untreated specimens.

* NSF Grant administered through Office of Research Services, College of Engineering.

4. PREPARATION OF SPINEL POWDER BY USE OF FREEZE DRYING, ITS CHARACTERIZATION AND CORRELATION WITH MICROSTRUCTURE

Chi-Shine Tao and Joseph A. Pask

Reactive magnesium aluminate spinel (MgAl₂O₄) powders were prepared by calcining freeze dried aqueous solutions of magnesium sulfate and aluminum sulfate hydrates.

The freeze dried powders were characterized in terms of their structure, dehydration kinetics, thermal reactions, particle size distribution, and particle aggregation. As a result of the understanding gained by the correlation of the freeze dried powders with the calcined spinel powders, the freeze drying process was modified in order to prepare freeze dried powders with the least amount of chemical segregation and calcined spinel powders nearly aggregate free. On modifying the freeze drying process by narrowing down the freeze dried particle size distribution by avoiding particle aggregation at the quick freezing and sublimation stages, homogeneous ultrafine spinel powders were obtained after calcination. The calcined powders were characterized in terms of their crystalline phases, residue sulfate content, crystallite growth during calcination and spectrographic analysis.

The spinel powder characterizations were correlated with their sinterability and sintered microstructures. Using the hot-stage scanning electron microscope, it was found that spinel powders of nearly single crystalline phase and the finest crystallite size have the fastest sintering rate. Increase of the packing homogeneity also increases the sintering rate of powders that have the same crystallite size.

The presence of strong spinel powder aggregates results in heterogeneous sintered microstructures which have large pores scattered in the dense matrix. Improvement of the freeze drying process as described above effectively eliminated this microstructural inhomogeneity. Powder packing homogeneity increases with increasing

green body density for powders with the same characteristics. Low green density powder compacts (less than 50% theoretical density) are less homogeneous and show exaggerated grain growth. Excess residue sulfate results in a grain boundary second phase for short-time sinterings. This second phase was removed by annealing in air at 1500°C, leaving pores along grain boundaries. Small amounts of residue sulfate form entrapped pores inside the grains during grain growth. It was found that long time vacuum calcination of the powder and secondary calcination in hydrogen remove the residue sulfate and thus reduce the entrapped pores. Different crystallite sizes generally affect the sintering kinetics.

Dry ball milling for a short period of time further reduces the aggregate size and increases the packing uniformity of the freeze dried powders in a desiccated condition. This procedure was found to be a more effective way to produce uniform calcined powders free of aggregates than ball milling the calcined spinel powders.

5. CRACK GROWTH IN GLASS SUBJECTED TO CONTROLLED IMPACTS*

William E. Snowden, M. W. Guinan and Joseph A. Pask

Crack growth in borosilicate glass plates subjected to controlled impacts was studied using high-speed streak photography. Target plates containing thermally-induced pre-cracks were impacted using a magnetic hammer system capable of providing impacts at known velocities and times. The maximum stress in the targets following impact increased approximately linearly with the velocity of the aluminum flyers. The duration of the stress waves generated on impact varied with the flyer thickness. The relation between stress pulse characteristics and crack growth was examined in an attempt to establish a criterion for fracture by stress waves. Critical impact velocities required for crack growth were determined for a range of experimental conditions. Corresponding stress histories at the crack front position in the target plates were calculated using finite-difference computer codes. Conditions for the onset of crack growth were found to be described by a least action law of the form

$$\int \frac{\sigma^2(t)}{E} dt = \text{constant},$$

consistent with recently proposed stress wave-crack interaction theories. The validity of a least action law for fracture by stress waves has not previously been established.

A number of other features of crack growth in glass plates subjected to controlled impacts were examined following impacts at velocities higher than the various critical values. These features included the formation of crack growth increments; crack acceleration, deceleration, and arrest; and crack branching. For the transparent targets used, streak photography proved to be an

invaluable method for recording crack velocity histories. Measured crack velocities ranged from approximately 400 m/sec to greater than 3000 m/sec. The highest observed crack velocity was significantly greater than any previously reported crack velocity in glass, a result attributed to the rapid load transfer provided by stress waves, the relatively low stress level which inhibited hackle formation and branching at lower velocities, and the method of observation. Crack branching at very high crack velocities was found to occur as a result of velocity-induced modification of the crack tip stress field in a manner compatible with the widely accepted view that branching depends primarily on the attainment of a critical energy release rate or stress intensity factor.

Fig. 1. Contact angle vs. oxygen partial pressure at 900°C for sodium borate glass on gold.
(XBL 7611-9837)

* Experiments were performed at Lawrence Livermore Laboratory, U.C.

6. WETTING AND REACTIONS OF B_2O_3 -CONTAINING GLASSES ON PLATINUM

Glenn A. Holmquist and Joseph A. Pask

Sessile drop experiments were conducted to analyze the wetting characteristics of molten B_2O_3 and B_2O_3 -containing glasses on Pt. In atmospheres free of carbonaceous gases, the contact angle for all glasses was $\sim 6^\circ$ and invariant under ambient pressures of 10^{-4} Torr to 1 atm for the range of 700 to 1000°C. Adsorption of carbon at the metal surface decreased the solid/vapor surface energy by ~ 50 ergs/cm² using a value of 80 ergs/cm² for borate glass, and increased the contact angle to 68° . Adsorbed carbon was removed from Pt by oxidation at ambient pressures of $\sim 10^{-1}$ to 5×10^{-3} Torr in the range 700 to 1000°C. Absorption of water vapor from the atmosphere by the glasses resulted in a reaction at the solid/liquid interface involving the reduction of hydroxyls in the glass structure by the Pt and the formation of metal oxides which saturate the interface. This reaction caused spreading of the glass and chemical bonding across the interface resulting in adherence.

7. WETTING BEHAVIOR OF B_2O_3 -CONTAINING GLASSES ON GOLD

Stephen T. Tso and Joseph A. Pask

Sessile drop experiments were performed to determine the wetting behavior of sodium borate glass on Au. The contact angle in the ambient pressure range of 10^{-8} to 10^{-5} atm was observed to be 46° under all conditions and the gold surface was found to be inert to carbon adsorption from carbonaceous vapor in contrast to platinum which showed carbon adsorption. The relation between the steady-state contact angle and the partial pressure of oxygen is shown in Fig. 1; the contact angle drops from 46° to 6° at pressures greater than $15 \mu\text{m Hg}$ at 900°C. This decrease in contact angle can be attributed to

the formation of an oxide layer on the Au surface which on solution by the glass caused a decrease in the Au/glass interfacial energy. Development of chemical bonding and adherence was the result.

In water vapor the glass drop vaporized more rapidly because of a change in its composition due to absorption of water vapor. Contact angles up to 60° indicated a decrease in the surface energy of the solid due to adsorption of gold. No adherence was observed indicating that the glass/metal interface was not affected; this effect was contrary to that experienced by glass in water vapor on Pt wherein a redox reaction occurred and adherence was developed. Summarizing, the adherence of borate glass to Au was due to saturation of the interface with gold oxide formed by oxidation of the metal surface by oxygen and subsequent solution by the glass; adherence to Pt was due to saturation of the interface with platinum oxide formed by a redox reaction at the interface between Pt and glass with absorbed water.

8. REACTIONS AND WETTING BEHAVIOR IN THE AuSi ALLOY- Al_2O_3 SYSTEM

Chisato Marumo and Joseph A. Pask

Changes of contact angle of a Au-31 at.% Si alloy on $\alpha\text{-Al}_2\text{O}_3$ (as received and heat treated in air at 1400°C) with temperature at a pressure of 10^{-5} Torr were determined (Fig. 1). An interface forms at $\sim 800^\circ\text{C}$ and the contact angle becomes $\sim 117^\circ$ for the heat-treated $\alpha\text{-Al}_2\text{O}_3$. An oxygen deficient surface forms in the range of ~ 950 to 1100°C with an increase of the surface energy of the solid and a drop of the contact angle to $\sim 78^\circ$. The formation of the oxygen-deficient surface resulted in an interfacial reaction with Si with the formation of reaction rings on the surface of Al_2O_3 and development of adherence of the drop to the surface. The surface of the as-received $\alpha\text{-Al}_2\text{O}_3$ specimen, on the other hand, undergoes

Fig. 1. Change in contact angle with temperature in the Au-31 at.% Si- α Al₂O₃ system using α Al₂O₃ as-received and heat-treated in air at 1400°C. (XBL 759-7214)

a dehydroxilation over the range of 800 to 1000°C which gradually merges with the oxygen-deficiency transformation up to 1100°C beyond which point behavior is similar for both sapphires.

9. RESEARCH PLANS FOR CALENDAR YEAR 1977

Joseph A. Pask

(a) Microstructure Development. Microstructure or character of a material determines its properties and behavior in specific environments. Interest in materials containing mullite, nominally with a composition of $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ has been regenerated. Despite the fact that SiO₂ and Al₂O₃ are the most abundant oxides in the earth's crust, detailed knowledge of the SiO₂-Al₂O₃ system is lacking. This situation has arisen because of the fact that stable and metastable mullites, which form depending on the details of the heating schedules, are not readily differentiated by x-ray diffraction techniques. In addition nucleation and growth phenomena of mullite and alumina under various conditions have not been completely understood and determined leading to erroneous phase equilibrium diagrams. Studies of this nature have been undertaken and will continue through the coming year. Determination of lattice parameters of stable and metastable mullites and correlation with solid solution compositions will be a primary objective. Developed principles should also be applicable to other oxide systems. Mechanisms of sintering are also being explored as a means of controlling microstructure.

(b) Mechanical Behavior. Studies are in progress to determine the effect of Cr₂O₃ additions on the nature of grain boundaries in polycrystalline MgO. These effects will be correlated with their mechanical behavior. MgO materials are of interest both as high temperature refractory materials and as specialized industrial ceramics. The nature of the grain boundary structure and composition are extremely critical in determining their mechanical behavior.

(c) Refractories for Coal Gasification Processes. National Science Foundation support for a project entitled, "Structure, Strength and Corrosive Resistance of Aluminum Silicate Materials," will continue through most of the calendar year. A project objective is to evaluate the capability of mullite and mullite-containing compositions to resist corrosion and erosion environmental conditions encountered in coal gasification processes. The specific research program is divided into two parts: high temperature mechanical behavior, and corrosion resistance to H₂-containing atmospheres. Studies are in progress on the development of microstructures based on mullite crystal size and distribution that will have improved behavior relative to these objectives.

Studies are also in progress to determine the fundamental mechanisms and kinetics of corrosion resistance to HF aqueous solutions and H₂ gas by silica-containing glassy materials.

(d) Interfaces. Interfaces between dissimilar phases (metallic or non-metallic) are critical in determining the behavior of composites, protective coatings, thin and thick films in electronic devices, and electrical lead-throughs. Studies are currently in progress on interfacial reactions and chemical interdiffusion in the area of chalcogenide glasses. Couples that are being used are based on various combinations of silver and arsenic selenides and sulfides.

10. 1976 PUBLICATIONS AND REPORTS

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Invitations

1. J. A. Pask, member of Visiting Review Committee, Materials Science Program, Ames Laboratory, ERDA, Iowa State University, Ames, Iowa, May 19-21, 1976.

2. J. A. Pask, Visiting Professor of Ceramic Science, Dept. of Engineering Materials, Federal University of Sao Carlos, Brazil, June 20-July 10, 1976.

3. J. A. Pask, Phase Equilibria and Transformations in the Alumina-Silica System, 2nd Brazilian Congress on Engineering and Science of Materials, Sao Carlos, Brazil, June 28- July 2, 1976.

4. J. A. Pask, Co-Chairman, International Symposium on "Ceramic Microstructures '76 with Emphasis on Energy Related Applications," Berkeley, California, August 24-27, 1976.

5. J. A. Pask, elected as Honorary Life Member of American Ceramic Society, 1976.

6. J. A. Pask, member of Visiting Review Committee, Materials Research Laboratory Program, Purdue University, Lafayette, Indiana, December 17-18, 1976.

c. High Temperature Reactions

Alan W. Searcy, Principal Investigator

1. CALCIUM OXIDES OF HIGH REACTIVITY^{*†}

Dario Beruto and Alan W. Searcy

A recent study of the kinetics of decomposition of calcite (CaCO_3) single crystals in vacuo showed that if the reaction was interrupted before completion a 30 μm layer of a poorly crystalline material was present between the undecomposed CaCO_3 and a layer of normal polycrystalline CaO .¹ It was hypothesized that the material of this 30 μm layer is a metastable form of CaO that transforms irreversibly to the stable polycrystalline oxide when the accumulated strain exceeds a critical level. If the hypothesis is true, then the principal product of decomposition in vacuo of calcite particles of diameter < 30 μm should be the metastable oxide.

We have now shown that this inference is correct, and we have demonstrated that not only this oxide, but also a highly crystalline oxide that is produced when large calcite crystals are decomposed in vacuo, reacts more vigorously with water than does the product of calcite decomposition in air or nitrogen.

The marked difference in particle morphologies that result from decomposition in vacuum and dry nitrogen are shown in Figs. 1 and 2. The high

Fig. 1. Scanning electron micrograph of CaO produced from decomposition of CaO_3 powders in dry nitrogen. (XBB 766-5107)

rates of reactivity of the oxides prepared in vacuo are primarily consequences of the high internal surface areas of the block-like products of vacuum decomposition. The blocks produced in vacuo have > 50% porosity,¹ yet the pores are too small to observe at X30,000. Pore diameters

Fig. 2. Scanning electron micrograph of CaO produced from decomposition of CaO_3 powder in vacuo. (XBB 766-5108)

probably average well under 0.1 μm so that solid state diffusion over only short distances is necessary for the hydration reaction. The rounded forms of the oxide particles prepared by decomposition in air must be a consequence of extensive condensed-phase diffusion, a process that would probably close the intraparticle pores.

^{*}This material appeared in Nature 263, 221 (1976).

[†]Support was provided by the Centro Studi di Chimica e Chimica Fisica, Universita di Genova, and ERDA.

1. D. Beruto and A. W. Searcy, J. Chem. Soc., Faraday Trans. I 70, 2145 (1974).

2. EFFECTS OF CARBON DIOXIDE AND SODIUM CHLORIDE ON THE SINTERING OF CALCIUM OXIDE

Alan W. Searcy, Richard M. Fulrath, Dario Beruto and Tushar Basu

Reactivities and particle morphologies of calcium oxide have been shown to be changed markedly if calcium carbonate is decomposed in vacuum rather than in air or dry nitrogen.¹ It appeared probable that carbon dioxide catalyzes the segregation of calcium oxide into rounded particles separated by pores of the order of microns when calcite is decomposed in air or dry nitrogen. Carbon dioxide might, therefore, be an effective catalyst for sintering calcium oxide and other oxides at lower temperatures than otherwise possible. Accordingly, calcium oxide powders were sintered under various experimental conditions in carbon dioxide and in air at 1000-1200°K.

Some differences in density and morphology were observed between similar powders heated in the

different atmospheres, but a commercial sample heated in air showed greater densification and particle rounding than the other samples, regardless of atmosphere. An impurity was probably responsible. This hypothesis was supported by observations that densification and rounding of particles of standard powders were catalyzed by 1% sodium chloride.

We hope now to investigate the hypothesis that carbon dioxide plus a salt may together promote calcium oxide sintering more effectively than either alone. It seems possible that calcium oxide may be effectively transported in some salts as the carbonate.

3. KINETICS OF ENDOTHERMIC DECOMPOSITION REACTIONS: III. EFFECTS OF THE POROUS SOLID PRODUCT

Alan W. Searcy and Dario Beruto

There has been no general theory for the kinetics of decomposition reactions. We have now published the first part of a general theory by describing the possible rate limiting chemical steps of a decomposition reaction and by deriving six limiting rate equations in vacuum in terms of those steps.¹ In the 1974 Annual Report of the Inorganic Materials Research Division of Lawrence Berkeley Laboratory, we summarized our findings of the predicted effects of product gas pressure on decomposition rates.² Now we have completed the general theory by deriving the effects of porous product layers on reaction rates when any of six limiting equations that govern the chemical steps is assumed to apply.

Two classes of dependence of rates on product layer thickness and on time are found. If the slowest chemical step of the reaction in vacuum is a step for the gaseous component of the reaction, the rate equations have the form

$$\frac{\alpha_B}{2cf} \ell^2 + \ell = \frac{V_A J_O}{f_A} t$$

where α_B is a measure of the excess free energy of the slowest chemical step; c , f , f_A , and V_A are constants of the porous barrier which can be measured or estimated; ℓ is the barrier thickness, and t is time. This equation predicts that the weight loss per unit area of surface may be constant at short time periods but will vary with $t^{1/2}$ when the barrier becomes sufficiently thick. If the slowest chemical step is a step for the solid reaction component, the equations predict that weight losses for thick barriers will vary with $t^{2/3}$.

Thus it should be possible to determine whether a step of the gaseous or the solid component of the reaction is slowest both by measuring the dependence of the decomposition rate on product gas pressure (as previously reported) or on time.

1. D. Beruto and A. W. Searcy, *Nature* **263**, 221 (1976).
2. 1974 IMRD Annual Report, LBL-3530, p. 188.

4. EXPERIMENTAL TESTS OF A SUGGESTED MECHANISM FOR DECOMPOSITION OF CALCITE (CaCO_3)[†]

Dario Beruto, Taghi Darroudi, and Alan W. Searcy

As one consequence of their general theory for decomposition reaction kinetics (see preceding article No. 3), Searcy and Beruto suggested¹ that their measured apparent enthalpies and entropies of activation for the decomposition of calcite *in vacuo*² could be most simply explained by the assumptions: (a) that the metastable oxide which they observed as a 30 micron thick layer between undecomposed calcite and a growing layer of the stable oxide has a heat of formation from the stable oxide of 7.5 kcal (the difference between the apparent activation enthalpy and the enthalpy of the equilibrium reaction) and (b) that the decomposition reaction has no excess enthalpy or entropy of activation. They pointed out that this mechanism could be tested by measuring the heat of formation of the metastable oxide or by measuring the equilibrium decomposition pressure of calcite to the metastable oxide.

Darroudi and Searcy have found that the equilibrium decomposition pressure cannot be measured for the reaction that produces the metastable oxide because when the carbon dioxide pressure is raised to within two orders of magnitude of the equilibrium pressure (in the practicable range of study near 1000 K), the stable crystalline oxide rather than the metastable oxide becomes the solid decomposition reaction product.

Beruto has successfully measured the heat of solution of the metastable oxide, which can be produced by decomposing small quantities of calcite of <30 micron diameter *in vacuo*. (See preceding article No. 1.) The heat of solution is about 3 kcal more positive than that of the stable oxide, so the metastable oxide has a heat of formation of +3 kcal, not 7.5 kcal. The observed kinetics of decomposition, therefore, cannot be explained by the simple mechanism suggested by Searcy and Beruto.

[†]Professor Beruto's research was supported by the Centro Studi di Chimica e Chimica Fisica, Università di Genova.

1. A. W. Searcy and D. Beruto, *J. Phys. Chem.* **80**, 425 (1974).
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5. THE EFFECT OF CARBON DIOXIDE ON THE RATE OF DECOMPOSITION OF CALCITE (CaCO_3)

Taghi Darroudi and Alan W. Searcy

As noted in the preceding article No. 4, when carbon dioxide gas is present at pressures in the range between 10^{-2} and 1 times the equilibrium pressure for decomposition of calcite, the solid reaction product is the stable crystalline form of calcium oxide. The theory of decomposition

reactions developed by Searcy and Beruto predicts that the rates will decrease linearly with increased pressure of the product gas if a chemical step for the gaseous component of the reaction is rate limiting, but will obey the relation

$$J = k \left(\frac{1}{P} - \frac{1}{P^\circ} \right) \quad (1)$$

where J is the flux of gas from the surface when the gas pressure is P , P° is the equilibrium decomposition pressure, and k is a rate constant, if the slowest chemical step is one of the solid reaction component. Measurements of flux of CO_2 from calcite as a function of CO_2 pressure, therefore, should provide insight into the decomposition mechanism. Two investigations have been reported of the effect of CO_2 pressure on the rate of decomposition of calcite, but in one study powdered samples were used and in the other flowing gas streams were used. Rates of decomposition of powders or of single crystals heated in flowing gases might be limited by gas phase diffusion rather than by a chemical step of the reaction. In order to obtain kinetic data with gaseous diffusion clearly eliminated as the rate limiting process, we have measured rates of decomposition of calcite single crystals at low enough temperatures so that the mean free path of vapor molecules is long even when the equilibrium decomposition pressure is maintained in the system.

We find, in agreement with the earlier results, that the flux is given by Eq. (1), so that either diffusion of calcium oxide in calcite or transfer of calcium oxide across the CaCO_3 - CaO interface is rate limiting. We hope that comparisons of the apparent activation enthalpies and entropies of the reaction with models will enable us to decide which is the case.

6. MEASUREMENT OF THE VERY SMALL CHANGES IN CALCITE COMPOSITION PRODUCED BY CHANGES IN CO_2 PRESSURE

Rama Shukla, David J. Meschi, and Alan W. Searcy

Most physical scientists have supposed that variations of compositions with partial pressures of the gaseous components of pseudo-binary solid phases that are formed by reaction of a solid metal oxide with a gaseous oxide such as carbon dioxide, sulfur dioxide, or sulfur trioxide, are too small to measure. We started, early in 1975, the construction of an apparatus for measurement of partial pressure variations and rates of partial pressure changes in such phases. This apparatus has proved capable of detecting and measuring the change in composition of calcite as a function of the partial pressure of CO_2 . The apparatus consists essentially of a vacuum furnace with a gas burette, CO_2 inlet and outlet assembly, pressure and temperature gauges, and a quadrupole mass spectrometer. The quadrupole is used to establish that gaseous impurities such as water are at negligible levels. Known quantities of CO_2 are introduced or removed from a known small

volume of the system that contains calcite. The volume of CO_2 that enters or leaves the calcite is calculated from the perfect gas law after correction for gas adsorption of the system in the absence of a sample.

Currently, we are able to measure changes in CO_2 content of the sample equivalent to $\sim 10^{-7}$ moles of CO_2 . This corresponds to compositional changes of $\sim 10^{-4}$ mole percent. Figure 1 shows a

Fig. 1. Variation of the mole fraction of carbon dioxide in solid calcite with the pressure of CO_2 at 773°K. (XBL 773-5190)

representative curve for P_{CO_2} vs. mole fraction of calcite obtained at 773°K. One interesting point to be noted is that the curve can be extended beyond the equilibrium phase boundary between calcite and calcium oxide. When nucleation occurs, the pressure rises to the equilibrium dissociation pressure. This aspect of decomposition reactions is to be further investigated by means of apparatus.

Measurements such as these should give new insight into partial molal thermodynamic quantities and defect chemistry for solids and may make possible the determination of the partial pressures of gaseous oxides present during formation of certain minerals in the crust of the earth.

7. THE TRANSPORT OF GASES THROUGH POROUS OXIDE BARRIERS

James A. Roberts, Jr. and Alan W. Searcy

An apparatus for studying the diffusion of gases over a wide range of pressures (1 to 10,000 μ) through porous materials over a wide range of temperature (room temperature to 1500°K) has been tested. The apparatus consists of a mass spectrom-

eter that has been modified with a gas inlet system that can supply gas to one side of a porous barrier mounted on a tube inside the mass spectrometer. Total flow rates through the porous barrier can be measured by observing the pressure drop in a calibrated volume of the inlet system. At the same time the composition of the gas emerging from the evacuated side of the barrier can be determined with the mass spectrometer. Being able to monitor simultaneously both the total flux and the gas composition is important for studies of gases that may undergo reactions (e.g., 1 dimer = 2 monomer or $\text{SO}_3 = 1/2 \text{O}_2 + \text{SO}_2$) as a result of passing through the barrier.

Under appropriate conditions gases may pass through porous materials by a combination of Knudsen effusion and surface diffusion. Experimentally the contributions to the total flux of the two mechanisms are separated by measuring the relative flow rates of pure helium and the gas under study.¹ Helium is assumed not to bond to the surface of solids at room temperature and above and thus passes through the barrier only by Knudsen flow. We have made several runs comparing the flow rates of He, Ar, CO_2 and SO_2 through alumina with pores of the order of 1 micron in diameter at temperatures between 300°K and 1000°C at pressures from 10 to 1000 μ . Under these conditions all the gases pass through only by Knudsen effusion.

A study of the kinetics of the decomposition of calcite indicated that during decomposition the CO_2 product was able to pass essentially unimpeded through the CaO decomposition product layer.² It was hypothesized that this rapid transmission of the CO_2 through the porous CaO took place by a combination of surface diffusion and Knudsen flow. To test this hypothesis we have passed He and CO_2 through barriers of CaO made by *in situ* vacuum decomposition of calcite discs. (The barrier must be made *in situ* since CaO reacts rapidly with water vapor in air.

The transmission of the barrier for helium and carbon dioxide appear both to be by Knudsen flow.

1. R. Ash, R. M. Barrer, J. H. Clint, R. J. Dolphin and C. L. Murray, Royal Society of London, Phil. Trans. 275, 255 (1973).
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8. EVALUATION OF PARTIAL AND INTEGRAL THERMODYNAMIC QUANTITIES FOR AN UNUSUAL DECOMPOSITION REACTION*

Alan W. Searcy and James A. Roberts, Jr.

Sometime ago we found¹ that on cooling in a limited temperature range near 1220°K, the partial pressure of Ga_2S_3 , one of two vapor species that are in equilibrium with gallium sesquisulfide (Ga_2S_3) solid, is increased, rather than decreased as normally expected. At the time we qualitatively

explained the anomaly as a consequence of a phase change at the temperatures concerned. We have now worked out a quantitative explanation.

The width of a miscibility gap associated with the phase change was found to be $X_S = 4 \times 10^{-3}$ at 1228°K,¹ and the variation of partial pressures with temperature at constant composition was known.^{1,2} From measurements of partial pressures as functions of composition when the mole fraction X_S of sulfur in the solid varied by 4×10^{-4} at 1237°K, we calculated the variation of Ga_2S_3 partial pressure with mole fraction at 1203°K. It was then possible to show that these data are consistent with a change of the composition of the high temperature phase boundary by 0.2 at.% sulfur between 1228°K and 1203°K (Fig. 1). From

Fig. 1. Partial phase diagram for the transition between high- and low-temperature forms of gallium sesquisulfide. (XBL 7610-7654)

the data we calculated partial and integral heats and thermal entropies of the phase transition:

$$\overline{\Delta H}_{\text{S}_2} = -200 \text{ cal}, \overline{\Delta H}_{\text{Ga}_2\text{S}_3} = 290 \text{ cal and } \Delta H = +90 \text{ cal}$$

for the integral change from low to high temperature phase.

* Forms part of a report accepted for publication in Science.

1. J. A. Roberts, Jr. and A. W. Searcy, Inorganic Materials Research Division Annual Report 1973, LBL-2299, April 1974, p. 187.
2. I. Y. Kashkooli and Z. A. Munir, High Temp. Sci. 4, 82 (1972).

9. RESEARCH PLANS FOR CALENDAR YEAR 1977

Alan W. Searcy

Most of our experimental studies during 1977 will be designed to further one or both of two objectives: (1) To test predictions of our theory for decomposition reactions and (2) To investigate the physical and chemical properties of the porous oxides that result from decomposition of carbonates and sulfates.

As mentioned at the end of preceding article No. 2 we hope to investigate the combined effects of CO_2 pressures and condensed state impurities on sintering of calcium oxide and perhaps other oxides. It is clear from comparison of Figs. 1 and 2 of preceding article No. 1 that calcium oxide can undergo a remarkable degree of condensed phase rearrangement if some as yet unclear set of conditions are established.

The studies of composition changes in calcite with CO_2 pressure, (preceding article No. 5), will be continued and perhaps extended to measurements of rates of change in composition. Such rate data would test whether the high rates of weight loss that are sometimes reported for the initial stage of decomposition reactions are consequences of degassing as usually supposed, or of changes in stoichiometry of the reactant solid phase.

Studies of the flow of gases through porous barrier that were described in preceding article No. 7 will be continued. One objective of these studies is to measure barrier transmission coefficients for comparison with our predictions of the influence of the porous product layers in decomposition reactions. A second objective is to seek means for separating gases by selective surface diffusion.

Efforts to prepare $\text{Al}_2(\text{SO}_4)_3$ in anhydrous and pore-free pellets have been unsuccessful, but we have found that the product of decomposing the hydrated sulfate to aluminum oxide has a surface area of $150 \text{ M}^2/\text{g}$ and is exceptionally reactive to water. We plan to investigate the reactivity of this material and of other vacuum-decomposed oxides toward SO_2 , SO_3 , and CO_2 . We hope to find an active oxide that is a more effective getter of sulfur oxides than have been the forms of the oxides so far discovered.

We will complete an investigation of the thermodynamics of SeS gas which was begun in 1976. We have prepared SeS by heating a mixture of indium sesquisulfide and indium sesquiselenide and have obtained preliminary measures of its stability.

Our theoretical efforts will probably be directed primarily to the development of new models for the thermodynamics of surfaces and of solutions. These thermodynamic models are important to our continuing theoretical interest in the kinetics of vaporization and decomposition reactions.

10. 1976 PUBLICATION AND REPORTS

Alan W. Searcy and Associates

Journals

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5. D. Beruto and A. W. Searcy, Calcium Oxides of High Reactivity, *Nature* **263** (5574), 221 (1976) (LBL-5155).
6. P. Mohazzabi and A. W. Searcy, The Effect of Porous Barriers on the Molecular Composition and Total Flux of a Reactive Gas Mixture, *J. Chem. Phys.* **65**, 5037 (1976).

LBL Reports

1. P. Mohazzabi and A. W. Searcy, A Porous Barrier Study of Mass Spectrometer Fragmentation Pattern of Lithium Fluoride, LBL-4806, 1976.
2. J. W. Roberts and A. W. Searcy, An Anomalous Temperature Dependence for a Decomposition Pressure, LBL-5459, 1976.

Technical Talks

1. Invited Principal Lecture, "Recent Advances in High Temperature Chemistry" at the Symposium, "Incontro di Studio Sulla Chimica Delle Alte Temperature," sponsored by the Laboratory of Chemistry, College of Engineering, University of Genoa and the Ligurian Section of the Italian Chemical Society.
2. Mass Spectrometer Studies of the Flow of Reactive Gases Through Porous Barriers, Alan W. Searcy, David J. Meschi, Pirooz Mohazzabi, and Gary Knutsen, National Meeting, American Chemical Society, San Francisco, CA, August 1976.
3. High Reactivity Calcium Oxides, Dario Beruto and Alan W. Searcy, Pacific Coast Regional Meeting, American Ceramic Society, San Francisco, CA, November 1976.
4. Anomalous Temperature Dependence for a Decomposition Pressure, Alan W. Searcy and James A. Roberts, Jr., Bay Area Conference on High Temperature Science and Technology, Berkeley, CA, November 1976.

d. Relation of Microstructure to Properties in Ceramics

Richard M. Fulrath, Principal Investigator

Introduction. The physical, chemical, and mechanical properties of ceramic materials are determined by the composition and the manner in which the composition is processed. Unlike metallic alloys which can be treated thermally, mechanically or combinations of both to significantly change their properties, the properties of processed ceramic materials are essentially unchanged by these processes. Therefore, to optimize the properties of existing ceramic materials and develop new materials required for advanced technology generated by raw material and energy shortages, research related to processing and the relation of processing to properties is essential to the progress of ceramic science.

This research effort is divided into four major areas. The first activity is concerned with the densification (sintering) of powder compacts with and without the presence of a liquid phase. A primary tool for these studies has been the MMRD developed capabilities in hot stage scanning electron microscopy. Both metallic and nonmetallic systems have been studied and include copper, nickel, uranium dioxide, aluminum oxide, iron-copper, and tungsten carbide-cobalt. Presently one study is concentrating on the effect of the stoichiometry of the solid phase when sintering with a liquid phase present. The titanium carbide-nickel system was chosen for this study because of the wide range of solid solution of titanium carbide. The second system under investigation is based on silicon nitride. Here the emphasis is again on liquid phase assisted densification with the liquid composition the primary variable.

The second major area of investigation is concerned with ferroelectric and piezoelectric ceramics in the lead titanate-lead zirconate system. This system offers a great challenge to understanding ceramic processing because of the high vapor pressure of lead oxide at elevated temperatures. Because of the volatility of PbO at high temperatures it is difficult to control the stoichiometry during processing ceramics in this system. The defects, primarily lead ion and oxygen ion vacancies, created by stoichiometric changes play a major role in determining the electrical properties. Therefore, combining measurements of electrical properties with processing parameter variations and basic studies on compound formation and PbO activity in this system has led to significant advances in developing a better understanding of processing and the role of the defect structure in determining the electrical properties. The present work encompasses two areas. One study is on the mechanism and kinetics of the formation of the compounds lead titanate and lead zirconate and their solid solutions. A second investigation is being pursued to establish the PbO activity in the lead oxide-aluminum oxide system and the equilibrium phase diagram. Two conflicting phase diagrams have been published in the literature.

The third major area of investigation is on thick film conductors, a major user of precious metals. The emphasis in this area has been to develop microstructures of thick film systems wherein the precious metal content can be significantly reduced or where base metals can be substituted for noble metals.

The last area of investigation is concerned with the mechanical properties of ceramics, especially the influence of porosity on the fracture toughness and strength. During the past two years this study has used lead zirconate titanate with induced porosity in a dense fine grained matrix. This work has been concluded and the emphasis now is being directed toward high temperature fracture toughness and strength of alumina and silicon nitride, two important ceramic structural materials.

The general theme of this total effort is to understand how microstructures are developed in the processing of ceramics and how the microstructure influences the properties.

1. SINTERING OF Al_2O_3 POWDER COMPACTS BY HOT STAGE SCANNING ELECTRON MICROSCOPY*

David N. K. Wang

Previous sintering studies on Al_2O_3 powder compacts have concentrated on the use of isothermal techniques. A complete analysis of sintering kinetics is unattainable due to uncertainties in the change of density of the compact with temperature and time in the initial heating period. The present work uses a nonisothermal constant heating rate technique to study the densification of MgO-doped Al_2O_3 powder compacts. Hot stage scanning electron microscopy was used to monitor continuously the linear dimensional changes of a powder compact throughout the densification process at various constant heating rates. Extensive studies on the microstructural evolution were made and correlated with the densification and grain growth kinetics.

Scanning electron fractographs of a prefired green compact are shown in the first picture of Fig. 1. This type of compact, having an initial density of 40% of theoretical, was used for the present work. Since voids contained in a green compact are determined by the packing of particles, the presence of agglomerates in the compact will make the pore size, location, and distribution more complex than assumed in models. A profound influence would be expected on both the rate of sintering and, more importantly, the residual porosity. As sintering proceeds, large pores will persist much longer than small pores.

Ceramographic examination clearly points to this occurrence. The other two pictures in Fig. 1

Fig. 1. Evolution of inter-agglomerate porosity at different degrees of sintering for Al_2O_3 powder compacts. Top to bottom: Green compact 40%, 85%, and 90% relative density. (XBB 761-826)

are the polished surfaces of the compacts sintered to 85% and 90% of theoretical density, respectively. The microstructure shown in the middle picture reveals that within individual agglomerates sintering occurs quickly, while a network of coarse porosity between them persists. The third picture shows the two dimensional inter-agglomerate boundary. This points out that not only the pores at the corners of agglomerates, but also the pores in the agglomerate boundaries will persist if early cohesion is not achieved during sintering.

Examination of densification rate vs. relative density curves in Fig. 2 reveals that the maximum value occurs at the same relative density (about 0.73), which is independent of heating rate and temperature. The occurrence of a maximum densification rate indicates that there must be microstructural changes during the densification process, which are vital to the densification rate.

Fig. 2. The densification rate of MgO -doped Al_2O_3 powder compacts as a function of relative density. (XBL 767-7259)

The effect of the evolution of pore phase on the densification rate can be understood by examining the development of microstructure of compacts during sintering. Figure 3 consists of six microphotographs which were taken from polished surfaces of fired compacts.

Compacts of 40% green density were heated at a rate of 4.6 °C/min from 800°C until the desired densities were achieved and then they were cooled by quenching. It is apparent that the average pore size increases and the number of pores decreases as density increases. Figure 3 also illustrates a transition region between 70% and 80% of relative density in terms of the uniformity of the distribution of small pores. (The inter-agglomerate pores are excluded from this observation since the high magnification used for these photographs allows coverage of only a few agglomerates). Microstructure developed at or below the relative density of 70% have a fairly uniform distribution of pores and microstructure developed at or above the relative density of 80% do not have a uniform distribution of pores. The nonuniform distribution of pores, i.e., the local variation in pore concentration, is usually more important than the range of pore size as far as the rate of densification is concerned. It is supposed that this local variation in pore concentration and the increase in average pore size are the reasons that the densification rate becomes highly density dependent. The occurrence of the maximum densification rate at a relative density of 73% (Fig. 2) coincides with the occurrence of a transition state (between relative densities of 70% and 80% in Fig. 3) concerning uniformity of pore concentration.

In addition to the evolution of pores the evolution of grain structure is also important to densification kinetics. Grain size is generally

Fig. 3. Evolution of the pore phase of MgO-doped Al_2O_3 (40% green density) powder compacts sintered at a rate of $4.6^\circ\text{C}/\text{min}$. The number appearing on the upper left hand corner of each photograph represents the value of relative density. (XBB 768-7114)

considered as a parameter which characterizes the diffusion pathlength for mass transfer during sintering. Previous studies on the grain growth kinetics in Al_2O_3 compacts have concentrated on the 90-99% density range. A cubic growth law and an activation energy of approximately 150 kcal/mole were determined.¹⁻³ Recently, Greskovich and Lay⁴ have studied the grain growth in very porous MgO-doped Al_2O_3 compacts. The temperature dependence of the process was not determined since only one temperature was used. In the present work, a more extensive study of grain growth kinetics was made. The effect of MgO dopant on the densification and grain growth of Al_2O_3 compacts was also studied. It was found that there is no effect of MgO dopant on either process until the critical density (73% of theoretical) is reached.

Using an empirical equation,

$$G^{m-1} \frac{dG}{dt} = \frac{K' \exp(-\frac{Q}{RT})}{kT},$$

a plot of $\ln dG/dt$ at a specific grain size, G , vs. $1/T$ gives a straight line of slope $-Q/R$. The activation energy for the grain growth process, Q , can be determined. Figure 4 gives the results obtained from powder compacts which were heated with three heating rates (2.5, 4.6 and $9.4^\circ\text{C}/\text{min}$). The activation energies were calculated as 95 kcal/mole and 150 kcal/mole for grain growth kinetics below and above the critical density, respectively.

Since the the rate of grain growth at a constant temperature is controlled by changes in volume fraction and size of pores (i.e., densification), there must be a relationship between the grain growth kinetics and densification kinetics

Fig. 4. Arrhenius plot of grain growth rate vs. $1/T$ for 0.1 wt% MgO-doped Al_2O_3 compacts with a 40% green density. (XBL 767-7253)

in terms of grain size and porosity. The relationship can be obtained from the equations which were formulated from the grain growth and densification processes.

For grain growth

$$G^{m-1} \frac{dG}{dt} = \frac{K' \exp(-\frac{Q}{RT})}{kT} \quad (1)$$

For densification⁵

$$\frac{dP}{dt} = \frac{K \exp(-\frac{Q}{RT})}{kT} P^n \quad (2)$$

Thus, after combination of Eqs. (1) and (2), and rearrangement, the relationship between grain size and porosity is:

$$G^m = k'' P^{1-n} \quad (3)$$

This equation predicts a straight line with a slope of $1-n/m$ in a plot of $\ln G$ vs. $\ln P$. The value of n has been determined to be 2.5 in the previous study⁵ by measuring the slope of straight lines from a plot of

$$\ln T \frac{dP}{dt} \text{ vs. } \ln P$$

at specific temperatures according to Eq. (2). Using $n = 2.5$ and $m = 3$ (determined from the grain growth study) in Eq. (3), a plot of $\ln G$ vs. $\ln P$ should give a straight line with a slope of $-1/2$. Indeed, as seen in Fig. 5, the results show a straight line with a slope of $-1/2$. This interdependence indicates that the grain growth in a porous compact during sintering is limited by the size and the volume fraction of pores in accordance with Zener's criterion.

Fig. 5. $\ln$ grain size vs. $\ln$ porosity for MgO-doped Al_2O_3 compacts of 40% green density heated at various rates. (XBL 764-6778)

* Abstracted from LBL-5763.

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4. C. Greskovich and K. W. Lay, Grain Growth in Very Porous Al_2O_3 Compacts, *J. Amer. Cer. Soc.* 55(3), 142 (1972).
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2. PREFERENTIAL DIFFUSION OF Ti^{4+} IONS IN THE FORMATION OF LEAD ZIRCONATE TITANATE SOLID SOLUTIONS

Y. Nakamura* and R. M. Fulrath

Previous work in this laboratory has shown that when powders in the micron size range of PbO , TiO_2 and ZrO_2 are mixed, compacted, and heated the compounds PbTiO_3 and PbZrO_3 form independently. PbTiO_3 starts to form at 450°C and PbZrO_3 at 700°C . After the individual compounds form they must interact to form a solid solution. This step is an extremely important one if homogeneous solid solutions are to be obtained in producing piezoelectric ceramics. X-ray analysis has not been

able to establish whether homogeneous solid solutions are obtained or if the counter diffusion of Zr^{4+} and Ti^{4+} can lead to crystallites with compositional variations. In order to study the interaction of $PbTiO_3$ and $PbZrO_3$ to form solid solutions high density pellets of $PbZrO_3$ and $PbTiO_3$ were formed, then crushed, and size fractionated. Pellets containing various mole fractions of $PbTiO_3$ and $PbZrO_3$ were formed by cold pressing and then heated to $1200^\circ C$ at $300^\circ C$ per hour in a controlled PbO atmosphere and allowed to furnace cool. The change in the diameter from the green pellet to the fired pellet was measured. Figure 1 shows

Fig. 1. Dimensional changes of pellets of various mixtures of $PbZrO_3$ and $PbTiO_3$ when heated to $1200^\circ C$ at $300^\circ C$ per hour and allowed to furnace cool. (XBL 773-5192)

the results for three particle sizes with varying composition. The end members $PbZrO_3$ or $PbTiO_3$ both showed shrinkage as would be expected when a powder compact is heated. The shrinkage was greater for the smaller particle size. When excess PbO was present that would promote liquid phase formation, even greater shrinkage was observed. $PbTiO_3$ also showed greater shrinkage than $PbZrO_3$. All these observations are in general agreement with theories of solid state or liquid phase sintering.

However, when mixtures of $PbTiO_3$ and $PbZrO_3$ were subjected to the same heat treatment the shrinkage was less than the end members and in the case of 37 to 44 micron diameter particles and 20 to 37 micron diameter particles an expansion was observed for all mixtures. Even a 50-50 mole percent mixture of one micron diameter particles exhibited nearly 6% expansion. Therefore, mixtures of $PbTiO_3$ and $PbZrO_3$ were formed into pellets in which large particles of one end member were

Fig. 2. Dimensional changes of pellets of various mixtures of $PbZrO_3$ and $PbTiO_3$ fired as in Fig. 1 but using different particle sizes. (XBL 773-5193)

combined with small particles of the other. As shown in Fig. 2 large $PbTiO_3$ particles combined with small $PbZrO_3$ particles showed shrinkage at small mole fractions of $PbTiO_3$ but expansion when the mole fraction was above 0.5. With large $PbZrO_3$ particles and small $PbTiO_3$ particles all mixtures showed approximately the same expansion. These results are interpreted as being due to the smaller Ti^{4+} ion diffusing faster than the larger Zr^{4+} and O^{2-} with Pb^{2+} ions having even higher diffusivity. Therefore, in a powder compact the $PbZrO_3$ particles grow as titanium, oxygen, and lead ions diffuse into the particle. This fast diffusion of Ti^{4+} relative to Zr^{4+} leads to an expanding skeleton when the solid solution formation is faster than the densification kinetics.

One diffusion couple run between $PbZrO_3$ and $PbTiO_3$ indicated Ti^{4+} as the faster diffusing specie.

This study points out the importance of particle size in producing homogeneous ceramic compositions.

* Guest scientist from the National Defense Academy, Japan.

3. INFLUENCE OF POROSITY ON THE MECHANICAL PROPERTIES OF LEAD ZIRCONATE-TITANATE CERAMICS*

Dipak R. Biswas

Because of the extensive work on the processing of lead zirconate-titanate (PZT) ceramics in this laboratory, it was selected as the material for study. In PZT polycrystalline ceramics (average grain size $2-5 \mu m$), the grain growth during processing was controlled by doping with one mole percent niobium oxide (PNZT). Spherical pores

(25-150 μm), of a controlled amount were introduced into the specimen using organic materials mixed with PNZT powders prior to forming pellets and sintering. Very fine pores (2-3 μm) were formed in PNZT ceramics by varying the sintering conditions namely green density, sintering temperature, and time. In this case the grain size was comparable to pore size. In both cases, the specimens were buried in $\text{PbZrO}_3 + \text{ZrO}_2$ packing powder and fired at 1100°-1200°C in one atmospheric pressure of oxygen. The packing powder technique was used to control PbO loss from the specimen during sintering.

Room temperature elastic modulus (E) was determined by the sonic resonance method. Once the exact resonance frequency was obtained, the elastic modulus was calculated from the resonant frequency, dimensions, and mass of the specimen. The results of elastic modulus vs. the volume percent porosity is shown in Fig. 1. The elastic

Fig. 1. Elastic modulus as a function of volume percent porosity for lead zirconate-titanate ceramics with pore diameters approximately equal to the grain size and pores approximately 50 times the grain size. (XBL 766-7028)

modulus for specimens with large pores follows a straight line relationship with porosity. The linear relationship of the form $E/E_0 = 1 - kP$ describes the experimental results. The value of k (constant) is found to be 2.5 for PNZT ceramics. The elastic modulus extrapolated to zero porosity is 11×10^6 psi. For fine pores (2-3 μm) the elastic modulus shows a slightly higher value compared to the material containing the same volume percent porosity but larger in size (110-150 μm). The natural frequency which was used to calculate the elastic modulus is theoretically correct only for materials without internal damping. The

damping capacity was measured from the width of half-maximum value of the resonance curve. The value was obtained by finding the resonant frequency at maximum amplitude and then locating the frequencies above and below the resonant frequency at which the maximum amplitude decreased to half of the resonant amplitude. Damping capacity was calculated from the differences of the two frequencies and the resonant frequency. The results are shown in Fig. 2. Damping capacity

Fig. 2. Damping capacity as a function of volume percent porosity for lead zirconate-titanate ceramics. (XBL 766-7027)

increases with increase in porosity. An interesting observation was that in PNZT specimens containing very fine pores (2-3 μm), generated by low temperature (1150°C) and short time firing, the damping capacity is approximately one third that for large pore specimens. It is even less than the extrapolated damping capacity value for a porosity free specimen.

In case of PNZT-fine pore specimens, it is suspected that some PbO rich liquid would be converted to crystalline PbO and PNZT during cooling and remains in the grain boundaries. Thus the grain boundary structure for PNZT-fine pore specimen may be different because of the presence of a small amount of PbO from the residual liquid phase. This will probably make the PNZT matrix more continuous. The dissipation of energy will be less for PNZT-fine pore specimen and reflected in low damping capacity and high elastic modulus.

Room temperature fracture toughness of PNZT ceramics was measured by the double torsion method.¹ The specimens failed catastrophically and the load at the point of failure was noted as P and the fracture toughness K_{IC} was calculated from the expression

$$K_{Ic} = P W_m \frac{3(1+\nu)}{W d_m^3}^{1/2} \quad (1)$$

where ν is the Poisson's ratio taken to be as 0.29 for PNZT ceramics, d , d_m and W_m are the specimen dimensions. The fracture toughness or the critical stress intensity factor depends only on the applied load P and not on the crack length. Figure 3 shows the K_{Ic} values against the volume

Fig. 3. K_{Ic} vs. volume percent porosity for lead zirconate-titanate ceramics. (XBL 766-7044)

percent porosity. K_{Ic} decreases with increase in porosity. The PNZT-fine pore specimen shows a slightly higher value. These higher K_{Ic} values for fine pore specimens can be explained from the fracture strength values of PNZT ceramics (Fig. 4). Note that in Fig. 4, the PNZT-fine pore specimen shows a definite higher strength value (up to 5% porosity) compared to PNZT-large spherical pores at the same volume percent porosity. The fracture strength is directly related to the load at the point of fracture. For PNZT-fine pore specimens the specimen failed at a higher stress and the load at the point of fracture is higher compared to PNZT-large pore specimens. As mentioned earlier the fracture toughness is not a function of crack length but it is directly dependent on the applied load at the point of fracture. Therefore, it is expected that PNZT-fine pore specimens will give higher fracture toughness as observed in Fig. 3. A typical microstructure of PNZT ceramics containing spherical and natural pores is shown in Fig. 5.

Thus for polycrystalline lead zirconate-titanate ceramics doped with niobium, small pores give a higher strength, elastic modulus and

Fig. 4. Fracture strength as a function of porosity for lead zirconate-titanate ceramics containing spherical and acicular pores much larger than the grain size and pores approximately equal to the grain size. (XBL 7512-10,007A)

Fig. 5. Microstructures of lead zirconate-titanate ceramics showing (a) large spherical pores (b) dense matrix of the ceramic in (a) and (c) the microstructure of a porous specimen where the pores are approximately equal to the grain size. (XBL 766-5596)

fracture toughness compared to ceramics with the same volume percent of large pores.

* Abstracted from LBL-5479.

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4. THERMAL ENERGY STORAGE USING SODIUM SULFATE DECAHYDRATE AND WATER*

Dipak R. Biswas

Water is commonly considered to be the most suitable material for thermal energy storage (TES) primarily because it is cheap and has a reasonably high heat capacity. An alternate means for TES is to use the latent heat of reaction. If the latent heat of reaction is large, this method has the advantage of making possible smaller systems (as illustrated in Table 1). As a practical matter, two criteria limit reactions that can be considered for such systems: (1) The reaction must occur in the temperature range of interest (normally for solar heating 30-50°C) and (2) The reacting material must be as inexpensive as possible.

On the basis of these considerations, the dehydration reaction of sodium sulfate decahydrate $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ looked promising, and considerable work has been done¹⁻³ using decahydrate as a TES material. It has been found² that the effective heat storage of the system degrades and is not reproducible after 5 or 10 cycles.

$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ decomposes peritectically on heating to 32.4°C to yield anhydrous Na_2SO_4 and a saturated solution of Na_2SO_4 in water. Any mixture of the saturated solution and anhydrous sulfate when cooled below 32.4°C can undergo the reverse reaction of solution. The decahydrate can form only as rapidly as water can diffuse through solid $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ to anhydrous Na_2SO_4 particles on which the decahydrate particles form. Peritectic solidification reactions⁴ are characteristically much slower than congruent solidification or eutectic solidification, and because the rate limiting process is solid state diffusion, stirring has no significant effect on the rate.

The purpose of this work was to describe a means of obtaining many of the advantages of the $\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ reaction while eliminating the solid state diffusion problem.

The partial equilibrium phase diagram² is shown in Fig. 1. Solid state diffusion can be eliminated as a reaction step by using a mixture of decahydrate and water as the starting material (68.2 W/O $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and 31.8 W/O H_2O). At 15°C (Point 2) this mixture consists of 58.1 W/O $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and 41.9 W/O solution of composition 10.6 W/O Na_2SO_4 and 89.4 W/O H_2O . When the temperature of the mixture is raised, the solubility of decahydrate increases.

Fig. 1. The equilibrium phase diagram for the H_2O - Na_2SO_4 system to 60 weight percent Na_2SO_4 from reference 2. (XBL 758-6939)

With the composition chosen, all the decahydrate dissolves when the system is heated above 32°C. The overall composition of the solution is 30 W/O Na_2SO_4 and 70 W/O H_2O . Now if the solution is cooled from 36°C (Point 5, Fig. 1), as it reaches the liquidus line (at 30°C), decahydrate crystals should begin to separate. As the temperature is further decreased, the system enters into a two phase region, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and liquid. The amount of each constituent can be easily calculated at any temperature by using the lever rule. The stored thermal energy in the system is released when the $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystals separate from the solution.

An experimental investigation was conducted to prove this concept and it was found that using the composition 68.2 W/O $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and 13.8 W/O H_2O , more than 25 cycles were successfully carried out and no separation of anhydrous Na_2SO_4 was observed.

* Abstracted from LBL-3998 Rev. Accepted for publication by the *Journal of the Interantional Solar Energy Society*.

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Table 1. Properties for storage of one million Btu heat using water or a sodium sulfate decahydrate-water system.

Materials	Density (lb/ft ³)	Sp ht (Btu/lb°F)	Heat of reaction (Btu/lb°F) Na ₂ SO ₄ ·10H ₂ O	Heat storage of million Btu with 20°F temperature limit	
				Mass(lbs)	Volume(ft ³)
Water	62.5	1.00	-	50,000	800
Na ₂ SO ₄ ·10H ₂ O	91.0	0.46	108	8,530	94
Na ₂ SO ₄ ·10H ₂ O and water	79.5	-	105	12,800 ^a	161 ^a

^a does not include the contribution from sp. ht.

5. RESEARCH PLANS FOR CALENDAR YEAR 1977

Richard M. Fulrath

(a) Sintering of Powder Compacts

Sintering studies on the TiC-Ni system will be carried out with the primary emphasis on variations in the Ti to C ratio of the solid phase. Experiments to date have indicated that the densification is greatly enhanced when a Ti/C ratio is greater than 1 in the TiC powder used. The ternary phase diagram indicates that a nickel-titanium liquid can form between 1050 and 1100°C and the few investigations to date suggest that if the Ti/C ratio is greater than one then the TiC can adjust its composition at sintering temperatures by expelling titanium and forming the stoichiometric carbide. The free titanium can react with nickel to form a low melting liquid and enhance densification. No carbide formers such as molybdenum are needed to obtain high density metal bonded carbides.

An investigation of the liquid phase sintering of Si₃N₄ has been initiated. The emphasis is on using silicate glasses as the liquid phase instead of adding oxide additions to form a liquid phase by reaction with the postulated SiO₂ layer on Si₃N₄ powder. The glasses chosen to date have been those that can be crystallized in an attempt to eliminate glassy phases at grain boundaries and subsequent degradation of high temperature properties.

(b) Piezoelectric and Ferroelectric Ceramics

Aluminum oxide refractories are extensively used in the production of lead zirconate titanate piezoelectrics. However, the activity of PbO in the PbO-Al₂O₃ system has not been determined and two conflicting phase diagrams for the system have been published. We are attempting to use the Knudsen Effusion techniques to establish both the PbO activity in the PbO-Al₂O₃ system and also to determine the phase diagram by this unique technique. This technique was very successful in studying the PbO-TiO₂-ZrO₂ system.

Work has also been initiated in studying the processing and properties of manganese doped lead zirconate-titanate ceramics. Manganese doping

should be very sensitive to the processing conditions because of the many valence states of manganese. The valence state of manganese additions to PZT will have a profound effect on the extrinsic defects and, therefore, the piezoelectric properties.

(c) Thick Film Conducting

It has been established that thick film conductors with one-half to one-third the precious metal content can be made by microstructure control by pretreatment of the glass phase. During the coming year we will optimize the glass composition for silver thick film conductors.

(d) Mechanical Properties of Ceramics

In the past the strength of ceramic materials have been determined either by compression loading or by bend tests for tensile loading. These relatively simple tests have been of considerable value to the ceramic fabricator in evaluating his processing techniques. However, in many new technological applications such as ceramics for gas turbines the design engineer requires other mechanical property data such as fracture toughness. We have initiated a program to determine both the room temperature and elevated temperature bend strength and fracture toughness of well characterized Al₂O₃ and Si₃N₄ produced in this laboratory.

6. 1976 PUBLICATIONS AND REPORTS

Richard M. Fulrath and Associates

Journals

1. L. Froschauer and R. M. Fulrath, Direct Observation of Liquid-Phase Sintering in the System Tungsten Carbide-Cobalt, J. of Materials Sci. 11, 142 (1975).

Papers Presented

1. Papers presented at the 29th Pacific Coast Regional Meeting of the Am. Ceram. Soc., San Francisco, October 31 to November 3, 1976.
 - 1a. R. M. Fulrath, Sintering from Theory to

Practice. (Invited keynote paper).

1b. D. R. Biswas and R. M. Fulrath, Elastic Modulus and Fracture Toughness of Porous PZT Polycrystalline Ceramics.

1c. Y. Nakamura, S. Chandratreya, and R. M. Fulrath, Anisotropic Mass Transport in Perovskite Structures.

1d. B. R. Powell and R. M. Fulrath, Phase Equilibria in the $\text{PbO-Al}_2\text{O}_3$ System Determined by Knudsen Effusion.

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4. R. M. Fulrath, Processing of Polycrystalline Piezoelectric Ceramics in the PZT System, ARPA/MRC Conference on Pyroelectric and Piezoelectric Materials, La Jolla, July 7-8, 1976.

LBL Reports

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9. D. Mentley, Microstructure of a Base Metal Thick Film Conductor, (M.S. Thesis), LBL-5176, June 1976.

10. D. R. Biswas, Influence of Porosity on the Mechanical Properties of Lead Zirconate Titanate Ceramics, (Ph.D. Thesis) LBL-5479, September 1976.

11. David N. K. Wang, Sintering of Al_2O_3 Powder Compact by Scanning Electron Microscopy, (Ph.D. Thesis) LBL-5763, November 1976.

e. Structure and Properties of Carbon Materials and Composite Materials

Robert H. Bragg, Principal Investigator

1. ELECTRICAL PROPERTIES OF GLASSY CARBON

R. R. Sexena and R. H. Bragg

We have completed the first round of our studies of the galvanomagnetic properties of glassy carbon (GC) samples heat treated for two hours each in the temperature range 1100-2800°C. The electrical properties studied include conductivity σ , Hall coefficient R_H and magneto-resistance $\Delta\rho/\rho$. Based upon the behavior of these properties two different regimes can be identified--above and below heat treatment temperature (HTT) 2000°C, henceforth named regimes I and II respectively. The summary of our results is as follows.

Hall Effect. As discussed elsewhere,¹ extensive R_H data were difficult to obtain because of experimental difficulties. For samples where reliable data could be obtained R_H exhibited only a weak temperature dependence at low magnetic fields, saturating as the field was increased to 50 kG. The variation in the number of carriers, derived from the saturation R_H value using the simple expression $R_H = 1/ne$, with HTT is shown in Fig. 1. A maximum around HTT 2000°C separates the two regimes. The general shape of the curve is in agreement with the results of the ESR measurements² on GC.

Fig. 1. Density of carriers in heat treated (two hours each) glassy carbon. (XBL 765-6911)

Conductivity σ . The conductivity was measured in the temperature range 10-300 K. For all the samples $\ln\sigma$ was found to be linearly related to the measurement temperature T over most of the temperature range. At the lowest measurement

temperatures σ saturates in regime I and exhibits a sharp decrease in regime II. The saturation value σ_0 in regime I was found to be equal to the σ value at the intercept of the $\ln\sigma$ vs. T line.

It was anticipated that more than one conduction mechanism will operate in GC since comparable density of extended and localized states were found in the ESR study.² For extended states the dominant scattering mechanism is diffuse boundary scattering because of the small crystallite size in GC. This gives rise to a temperature independent contribution σ_0 to σ . For localized states hopping conduction is expected.

In regime I, the intercept σ_0 is the temperature independent contribution to σ , but not obviously so in regime II. However, assuming σ_0 to be this contribution in regime II as well, $\ln(\sigma - \sigma_0)$ was found to linearly related to $T^{-1/4}$ for all the samples. This is the hopping conduction contribution to σ following Mott's $T^{-1/4}$ law. To analyze the anomalous behavior at low T in regime II, the extrapolated hopping contribution σ_{hop} was subtracted. The remainder σ_K was found to be linearly related to $\log T$ as shown in Fig. 2. This behavior is characteristic of Kondo systems in the temperature range above the Kondo temperature T_K .³ The saturation value (Fig. 2) is found to be the same as σ_0 thus validating the initial assumption.

Fig. 2. Kondo contribution to conductivity in heat treated glassy carbon. (XBL 7611-7819)

To conclude this section we have shown that σ in regime I consists of a temperature independent contribution σ_0 and a hopping contribution following $T^{-1/4}$ law. In regime II there is an

added resistance at low T due to scattering related to the Kondo effect of the localized spins.

Magnetoresistance. As reported earlier,⁴ the negative magnetoresistance in GC can be analyzed in terms of the variable $\lambda H/T$, where λ is a temperature dependent adjustable parameter. We studied the temperature dependence of λ and were thus able to isolate the appropriate variable for analyzing $\Delta\rho/\rho$. In regime I, $\Delta\rho/\rho$ has been found to be a single valued function of $H/T^{1/2}$, but departure from this behavior is seen in regime II.

It can be shown by a simple analysis in terms of Kondo spin-flip scattering that $\Delta\rho/\rho \propto -m^2$, where m is the effective magnetic moment per spin.¹ Thus we have plotted $|\Delta\rho/\rho|^{1/2}$ against $H/T^{1/2}$ on a log-log plot in Fig. 3, which also shows the

Fig. 3. Negative magnetoresistance in soft carbons compared with present investigation. (XBL 768-7382)

same behavior in some published data on soft carbons. In regime II all the data do not fall on the same curve and a more complicated analysis seems to be required. In regime I $|\Delta\rho/\rho|^{1/2}$ for low values of the variable, implying a $T^{-1/2}$ behavior of the susceptibility χ ($= m/H$). Anomalous behavior of χ is expected on the metallic side of the insulator-metal transition³ known to take place in carbons around $H_{TT} 700^\circ\text{C}$.¹ We have also analyzed published $\Delta\rho/\rho$ data in semiconductor systems on the metallic side of the transition to show that $H/T^{1/2}$ is indeed the appropriate variable.¹ A paper on the magnetoresistance investigation has been submitted to Philosophical Magazine, and a paper on the conductivity and Hall Effect has been submitted to J. Non-Crystalline Solids.

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2. X-RAY STUDIES OF LINE PROFILE IN GLASSY CARBON

S. Bose, R. R. Saxena and R. H. Bragg

Our studies of x-ray diffraction from glassy carbon (GC) have shown that in a disordered, highly porous material the small angle x-ray scattering intensity makes a significant contribution to the wide angle x-ray diffraction profile. GC has a large number of voids (about 40% by volume) which account for the reduced density (1.5 g/cm^3) compared to graphite (2.25 g/cm^3) and give rise to very prominent small angle x-ray scattering (SAXS). The SAXS intensity in GC persists in appreciable amounts up to diffraction angles (2θ) normally considered to be part of wide angle x-ray diffraction region. This leads to abnormally large background intensity at low angles and asymmetric peaks in as obtained x-ray diffraction profile from heat treated GC samples, as shown in Fig. 1.

Fig. 1. Glassy carbon XRD pattern (uncorrected). (XBL 771-7398)

To obtain meaningful parameters to characterize the material it is important to correct for all extraneous intensity contributions and obtain the true interference function prior to analysis. The correction procedure is as follows: First, the full diffraction pattern, including the SAXS is recorded in transmission and reflection, and the transmission data is used to correct the reflection data at the smallest angles. Next the background intensity due to incoherent scattering is subtracted from the observed x-ray diffraction intensity profile. To calculate the proportionality constant for this it is assumed that the intensity at a high enough angle ($2\theta \sim 120^\circ$) where there is no graphite-type peak is due totally to incoherent scattering. The extrapolated SAXS intensity from the intensity dependence on $\sin \theta/\lambda$ in the Porod region is then subtracted. In this region the intensity is directly proportional to $(\sin \theta/\lambda)^n$ and the extrapolation is done using a plot of $\log I$ vs. $\log (\sin \theta/\lambda)$. After this step the Lorentz-polarization factors and the atomic scattering factor f^2 are divided out to obtain the true interference function which is normalized to

the maximum peak intensity. A computer program has been written to perform this correction procedure.

The corrected profiles corresponding to Fig. 1 is shown in Fig. 2. As is expected, a symmetric

Fig. 2. Corrected line profile for GC 2700 and GC 1200 (normalized independently). (XBL 771-7399)

(002) profile is obtained and on either side of this peak the intensity drops down to zero. The latter is important because it demonstrates that the background has been removed correctly. Also the corrected data show a far better resolution of the (10) band and the (004) maximum, thus permitting an estimate of L_a from peak broadening, and estimates of d_{002} from both the 002 and 004 reflections. The effect of these corrections on various structure parameters is tabulated in Table 1.

It can be seen that the effect of the corrections is largest for the material heat treated to

the highest temperature, and this is precisely the region where accurate data are required for studying the kinetics of graphitization. It appears that previous estimates of activation energies based on L_c data are in error and must be recalculated.

3. KINETICS OF GRAPHITIZATION OF GLASSY CARBON

R. R. Saxena and R. H. Bragg

We have studied the kinetics of graphitization process in glassy carbon (GC) using the structure parameters obtained from wide angle x-ray diffraction studies. The x-ray data were corrected as described in the preceding article No. 2 and three parameters were calculated. The variation of d_{002} , L_c and L_a with HTT for GC samples heat treated for two hours each is shown in Fig. 1. Three separate regions can be

Fig. 1. Structural parameters vs. HTT (2 hr) for glassy carbon. (XBL 765-6899)

Table 1.

	1200°C - 1 hr.		2700°C - 2 hrs.	
	From corrected profile	% error for uncorrected profile	From corrected profile	% error for uncorrected profile
d_{002} Å	3.54	1.7	3.41	1.7
L_c Å	11.8	1.3	24.8	21.5
L_a Å	33.0	7.0	47.3	16.4
$d_{002} = \lambda/2\sin\theta_m$; $L_c = 0.45\lambda/\Delta(\sin\theta_c)$; $L_a = 0.92\lambda/\Delta(\sin\theta_a)$.				

identified, and we have named these according to the characteristic process we believe to be taking place.

I. Dehydrogenation ($\text{HTT} < 1500^\circ\text{C}$). In this region L_c , L_a increase with HTT while d_{002} decreases. Hydrogen evolution is still going on and our mass spectrometer experiment has confirmed the presence of H_2 evolution up to 1150°C .

II. Strain Relief ($1500^\circ\text{C} < \text{HTT} < 2300^\circ\text{C}$). In this region L_c , L_a increase with HTT while d_{002} remains constant at 3.44 Å. This value of d_{002} has been used as the interlayer spacing for turbostratic carbons.¹ We believe that the major process in this region is strain relief which leads to a slight increase in L_c , L_a .

III. Graphitization ($\text{HTT} > 2300^\circ\text{C}$). In this region the glassy carbon structure can be described in terms of a randomly oriented small crystallite model, whereas an entangled lath-like structure is the more appropriate description in previous regions. It is to be noted that even at 2800°C , the d_{002} value is far from the ideal graphite value, and the reason for this is the thermodynamic stability of the disordered structure.²

To study the process of graphitization GC samples were heat treated for various time intervals at a few fixed temperatures. The variation in L_c with time at fixed HTT is shown in Fig. 2. These data can be analyzed using the "superposition" technique. Whereas the curves for $\text{HTT} > 2300^\circ\text{C}$ in Fig. 2 can be superimposed, the

Fig. 2. Kinetic data of L_c for glassy carbon. (XBL 765-6901)

curves for lower HTT exhibit a different behavior. This is in agreement with our belief of a different process taking place in Region II which

appears to be much slower. Taking GC 2700 series as the reference other plots in Region III may be translated onto a master plot as shown in Fig. 3.

Fig. 3. Superposition of L_c kinetic data for GC. (XBL 765-6902)

From the shifts needed to superimpose curves onto the master composite plot the activation energy of graphitization can be obtained as shown in Fig. 4. The value obtained is 200 ± 30 kcal/mole.

Fig. 4. Arrhenius plot of L_c data for GC. (XBL 765-6903)

Similar analysis of L_a data was difficult due to scatter in the data, which arises from interference of (004) peak. However, L_a data at 75% width of the maximum could be analyzed to obtain an activation energy of 225 ± 30 kcal/mole. The

combined estimate is 215 ± 40 kcal/mole. The d_{002} were not precise enough to be independently analyzable, but the changes in d_{002} values are consistent with the estimated activation energy.

The activation energy obtained is close to but somewhat less than the value commonly accepted for vacancy diffusion in graphitic carbons. This could be due to an excess concentration of point defects in the disordered structure. "This seems a reasonable assumption, and some experimental evidence is provided by the observation of Delhaes and Merchand on the relative ease of introducing substitutional boron into disordered graphitizing carbons compared with the difficulty of introducing it into graphite."¹ A paper on our results has been submitted to carbon.

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4. KINETICS OF VOID GROWTH IN GLASSY CARBON

Sudhangshu Bose and R. H. Bragg

Glassy carbon (GC) is a representative of a class of carbons known as "hard" or "non-graphitizing" carbons. Its microstructure is featureless, but its relatively low density (~ 1.5 gms/cm³ compared to 2.25 gms/cm³ for graphite) together with strong small angle x-ray scattering (SAXS) indicates the presence of voids in GC. However GC has negligible gas absorption and permeability suggesting that the voids are closed. The void sizes have been determined by a number of investigators and have been found to be between 10 Å and 40 Å. The effect of heat treatment is to increase the size of the voids and reduce their number. However, the kinetics aspect of this void growth was recognized only recently by Biswal and Bragg.¹ Since the graphitizability or rather the nongraphitizability of GC has been found to be related to the voids and since void growth is likely to unravel the mechanism of transformation, work on kinetics of void growth in GC has been undertaken.

Measurement of density of GC heat treated to various temperatures (HTT) for various times (HTt) indicated that at any HTT, density decreased with (HTt) showing pore growth. Since the SAXS technique would be ideal for the pore sizes that GC has and for $\Delta Z \approx 6$ (atomic number difference between carbon and pores), the scattering will be intense. SAXS patterns were run for samples heat treated between 1700°C and 2700°C for various HTt. A representative intensity distribution is given in Fig. 1. Guinier plots of $\ln I$ vs. h^2 (where $|h| = 4\pi \sin \theta / \lambda$, 2θ = scattering angle and I = intensity at 2θ) gave the radius of gyration of voids R_G . A representative 'Guinier' plot is shown in Fig. 2 and R_G 's obtained from these plots are shown in Fig. 3.

Fig. 1. SAXS intensity from GC. (XBL 773-5197)

Fig. 2. "Guinier" plots of small angle scattering data from GC. (XBL 773-5198)

In preceding article No. 3 it was found that the kinetics of "graphitization" of GC can be characterized by an activation energy of about 200 kcal/mole. The primary purpose of this work is to determine if the structural parameter R_G or some other, such as specific surface area is

Fig. 3. Kinetics of void growth in GC.
(XBL 773-5174)

capable of the superposition analysis of d_{002} and L_c and L_a used by most investigators. Preliminary calculations based on the data of Fig. 3 indicate that the activation energy for void growth is the same as that for crystallite growth. An effort is also being made in relating other physical properties of GC to the growth of voids in it.

1. M. M. Biswal and R. H. Bragg, Void Growth in Glassy Carbon, 12th Biennial Conference on Carbon, Pittsburgh, Penn., August 1975.

5. SMALL ANGLE X-RAY SCATTERING BY PYROLYTIC GRAPHITE

Sudhangshu Bose and Robert H. Bragg

Small angle x-ray scattering (SAXS) from oriented ellipsoids of revolution has been analyzed theoretically by Bragg and Hamzeh.¹ The calculated intensity depends on the size and orientation of the voids through the relation

$$I(hH) = nI_e(\rho V)^2 \left[3 \frac{\sin(hH) - hH \cos(hH)}{(hH)^3} \right]^2$$

where $H^2 = a^2 \sin^2 \gamma + b^2 \cos^2 \gamma$; a , b are the semi-major and semi-minor axes of the ellipsoid of revolution (b being revolution axis) respectively; γ is the angle between scattering vector $\vec{h}$ ($|\vec{h}| = 4\pi \sin \theta / \lambda$, 2θ = angle of scattering) and b ;

n = number of ellipsoids irradiated, each having electron density ρ and volume V ; I_e = the intensity scattered by a single electron.

Thus in the "Guinier" approximation as $h \rightarrow 0$,

$$I(hH) = nI_e(\rho V)^2 \exp \left\{ -\frac{1}{3} h^2 (3/5 H^2) \right\}$$

where the "Guinier" radius is $\sqrt{3/5} H$.

In Porod approximation as $h \rightarrow \infty$,

$$I(hH) = nI_e \frac{2\pi\rho^2}{h^4} \frac{9V^2}{4\pi H^4}$$

which in the infinite slit height approximation becomes

$$I(hH) \propto \frac{1}{h^3 H^4}$$

Thus,

$$[h^3 I(hH)]^{-1} \propto (a^2 - b^2) \sin^2 \gamma + b^2$$

The foregoing analysis was made because there was no theory available to characterize anisotropic small angle scattering observed in pyrolytic graphite, GC.

Pyrolytic graphite is characterized by oriented pores which appear circular viewed normal to the deposition surface and elliptical viewed parallel

Fig. 1. Porod plots of small angle scattering by pyrolytic graphite.
(XBL 766-7066)

to the deposition surface. It is therefore an ideal material to test the theory. Experimental procedures and preliminary results in the 'Guinier' region was presented in the previous annual report (1975). Since then data were obtained in the asymptotic Porod region. The Porod plots of $\ln I$ vs. $\ln h$ for γ between 0° and 90° are straight lines with slope -3 as shown in Fig. 1. Figure 2 is a plot of $h^3 I$ vs. h^2

Fig. 2. Plots showing -3 slopes in Porod region. (XBL 773-5199)

which gives the value of $h^3 I$ in the asymptotic region. This limiting value of $h^3 I$ has been plotted against $\sin^2 \gamma$ and, as shown in Fig. 3,

Fig. 3. Verification of asymptotic dependence of $I(h)$ on γ . (XBL 766-7065)

the data are linear except at the highest value of γ . Thus, the intensity of SAXS from PG seems to obey the asymptotic law predicted by the theory of Hamzeh and Bragg. Data from the Guinier region provides values $2a = 228\text{\AA}$ and $2b = 152\text{\AA}$. Thus $b^2/a^2 - b^2 = 0.80$. Data in the Porod region (see Fig. 3) gives a value of 0.77 in reasonable agreement with that given by Guinier region. These results were presented at the Carbon Conference in Baden-Baden.²

A departure from straightline at larger values of γ may be due to the effect of slit smearing of the anisotropic intensity distribution. An analysis of this anisotropy needs data in two dimensions. Work is in progress in this direction in conjunction with Dr. R. W. Hendricks at Oak Ridge National Laboratory.

1. F. M. Hamzeh and R. H. Bragg, J. Appl. Phys. 45, 3189 (1974), LBL-1874, August 1973.
2. S. Bose and R. H. Bragg, Duetshe Keramische Gesellschaft, Carbon '76, 201, Baden-Baden.

6. TEXTURE AND INTERPHASE RELATIONSHIPS IN DIRECTIONALLY SOLIDIFIED Al-CuAl₂ EUTECTIC ALLOY

Leopoldo Valero and Robert H. Bragg

The aluminum-copper eutectic alloy when unidirectionally frozen will solidify as parallel lamellae if the solidification parameters are controlled appropriately. These variables are the temperature gradient at the solid/liquid interface (G), the growth rate (R), and the concentration of impurities (C_0). The ratio G/R must be high enough to compensate for any impurity present which causes constitutional supercooling. This is important because a constitutionally supercooled layer at the advancing solid/liquid interface stabilizes a cellular rather than a planar interface which leads to the formation of undesirable eutectic colonies.

Ideally certain crystallographic directions in one or both phases should lie parallel to the growth direction and a definite interphase relationship should exist everywhere throughout the grown ingot. As grown these directionally solidified eutectics are not perfect duplex single crystals and are best described in terms of a strong preferred orientation. The objective of this work is to determine to what extent the texture, orientation relationships and lamellar spacing λ are determined by the solidification parameters.

An ingot solidified in our laboratory typically weighs about 100 g, is 8 in. long and has a cross section of about $1/2$ by $3/4$ in. Usually the middle 4 in. section has a regular lamellar microstructure, but the end where freezing begins consists of randomly oriented grains and the portion which freezes last has a fan-like arrangement of crystal aggregates. The center portion is taken as representative of steady-

state conditions. Micrographs of this portion show the expected two phases: K (essentially Al-5.7% Cu) and θ (CuAl_2). As solution heat treated K is FCC with $a_0 \approx 4.04 \text{ \AA}$, and θ has a complex body centered tetragonal structure with $a_0 = 6.04 \text{ \AA}$ and $c_0 = 4.86 \text{ \AA}$ (see figures).

A literature survey on the crystallography of the Al-CuAl₂ eutectic has shown disagreement among different investigators. The experimental conditions have been quite different in each case and not a single work has been repeated either by preparing the specimen in the same manner or by using the same technique for texture determination. Recently B. Cantor¹ and G. A. Chadwick have stated that discrepancies are due to variations which are present in the lamellar plane orientation and that an invariant relationship does not exist. It is our belief that the disagreement between investigators is due to the fact that kinetic factors are determining.

The $(111) \text{ Al} \parallel (211) \theta$ relationship at the interface has been discussed by R. W. Kraft² in terms of atomic positions and atomic density in the stacking sequence of the two planes involved. It was observed that in the θ phase the stacking sequence parallel to $\{211\}$ is very unusual and this fact may account for the tendency of the $\{211\}$ planes to be interfacial planes.

To physically visualize the (211) plane we have constructed a scale model of the θ phase (Fig. 1a) and verified the fact that in this plane four layers of aluminum atoms are grouped together and that it is possible to consider these four layers as just one single plane as it was suggested by Kraft (Fig. 1b). A scale model of the k phase was also built (Fig. 1c) and now we are able to explore other possible relationships between the two phases by a direct three-dimensional examination (Fig. 1d).

For the texture and interphase relationships determination we have recorded some preliminary x-ray diffraction data from a specimen grown at a rate of 9.24 cm/hr. A 1 in. long sample was cut from the ingot and machine shaped as a rectangular parallelepiped with its sides parallel to the growth direction. Reflection data were obtained from the top, side and transverse sections. Now that we know which planes are strongly reflected, data to construct pole figures will be collected. The method described by R. H. Bragg and C. M. Packer³ will be used to obtain data in blind regions of the pole figures, to make the necessary corrections for absorption, and to normalize the data to "times random units." The texture of the Al-CuAl₂ eutectic will be determined at different growth rates to afford a test of constancy of interphase relationships.

Fig. 1. (a) Scale model of the θ -phase unit cell (body centered tetragonal). (b) The θ -unit cell oriented with the (211) plane horizontal. (c) Scale model of the k-phase (face centered cubic). (d) Illustration of the interfacial relationship $(111) \text{ Al} \parallel (211) \theta$. (e) The two-scale models placed together for comparison.

[(a), (b), (c), (XBB 773-1907); (d), (e), (XBB 773-1908)]

1. B. Cantor and G. A. Chadwick, Journal of Crystal Growth 23, 12 (1974).
2. R. W. Kraft, Trans. AIME 224, 65 (1962).
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7. THERMAL AND ELECTRICAL PROPERTIES OF DIRECTIONALLY SOLIDIFIED Al-Al₂Cu EUTECTIC ALLOY

D. Baker, S. Justi and R. H. Bragg

Directionally solidified eutectics are a class of natural (in situ) materials. In composite materials usually a soft matrix (in this case: Al-5.7% Cu) is reinforced by an aligned fibrous or lamellar second phase (in this case: Al₂Cu). It is of interest to calculate the properties of such composite materials. A first approximation can be obtained by using the "Rule of Mixtures" (RoM), assuming that the properties of the constituents and the volume fractions are known. The RoM, however, does not take "special characteristics" into account. For the case of the directionally solidified Al-Al₂Cu some of those "special characteristics" are:

- the phase geometry (e.g., the alignment of the phases, different interlamellar spacings λ),
- growth defects (e.g., colonies, bands, additional lamellae),
- the orientation relationship between the k- and the θ -phases (see preceding article No. 6),
- aging effects which might occur in the k-phase.

Following the theory of Hashin,¹ there is a general correspondence of the electrical, thermo-physical and elastic properties of aligned composite materials. Due to the limited sample size it is in most cases easier to carry out measurements of the electrical resistivity and/or thermal expansion instead of determining the yield strength through tensile tests and the elastic modulus through tensile or ultrasonic measurements.

If Hashin's theory proves true, we will be able to predict the yield strength and the elastic modulus through measurements of the thermal expansion and the electrical resistivity. On the basis of these measurement we can determine the deviation from the RoM, and by using the same method of correction for the RoM we will be able to calculate the yield strength and elastic modulus of the composite.

We chose the Al-Al₂Cu eutectic as a model because it is relatively easy to grow, and much is already known about this system and its components.* The aligned composite and the k-phase are obtained by directional solidification in a horizontal resistance heated furnace at temperature gradients G ahead of the solid/liquid

interface of about 45°C/cm. The interlamellar spacing λ is varied by freezing the eutectic at different rates, R . According to theory the relationship obtained with an appropriate G/R is

$$\lambda^2 R = \text{constant}.$$

Metallographic investigation of the frozen ingot, which is 25.4 cm × 2.54 cm × 1.43 cm, normally shows three different regions. Starting with the end first frozen, we find a multigrain structure, which although aligned with the growth direction is not useable for experimental purposes. After a distance of about 5-6 cm a one grain structure (Fig. 1a), occasionally a two grain structure (Fig. 1b) is found. The lamellae show a slight

Fig. 1. Optical micrograph of directionally solidified Al-Al₂Cu eutectic (side view). $G = 44$ °C/cm, $R = 9.24$ cm/h, magnification 600x. (a): one grain microstructure (b): two grain microstructure. (XBB 773-1909)

angle of 10-15 degrees to the growth direction in the side view due to the heat flow conditions of the furnace. The last 5-6 cm of the ingot also shows an irregular structure and is not used.

The determination of the interlamellar spacing λ for the center region shows that for the ingots grown to date the $\lambda^2 R = \text{constant}$ relationship is obeyed (Fig. 2), and that the data found are in agreement with those found in the literature.²

Specimens for the thermal expansion experiments are cut from the center region in three orthogonal directions with the lamellae as coordinates (Fig. 3). The thermal strain $\epsilon_{th} = \Delta l / l_0$ with $\Delta l = l - l_0$ and the temperature difference $\Delta T = T - T_0$ are measured using a standard push rod dilatometer which is calibrated with high purity (99.999%) Al and Cu, and a Pt-10% Rh thermocouple. The mean thermal expansion coefficient α_{th} can be calculated through the equation

$$\epsilon_{th} = \alpha_{th} \Delta T.$$

Fig. 2. Interlamellar spacing λ vs. growth rate R for directionally solidified Al-Al₂Cu eutectic. (XBL 773-5201)

Fig. 3. Coordinates for thermal expansion measurements (idealized crystal). (XBL 773-5200)

Preliminary results suggest that the thermal expansion behavior of the aligned eutectic is anisotropic, but more data are necessary before conclusions can be drawn.

The electrical resistivity measurements have not been started yet. We plan to make use of the 4-probe resistivity measuring apparatus, which has been tested earlier.³ We will, however, extend the measurements to the three orthogonal directions. We are currently working on the problem of improving the output rate of our solidification furnace. Of a 25 cm long ingot only about 40% of the material has an acceptable aligned microstructure. We are testing both seeding and back and forth melting techniques to favor a one grain structure over a long distance, so that samples from the same ingot

can be used for measurements of the thermal expansion, electrical resistivity, elastic modulus and tensile properties.

We wish to thank Professor Alfred Yue, UCLA, for a portion of an ingot of pure Al₂Cu material which will be most useful for our experiments.

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8. RESEARCH PLANS FOR CALENDAR YEAR 1977

Robert H. Bragg

The electrical properties and structural parameters in glassy carbon in the HTT region below 2300°C will be investigated at closely spaced temperature intervals to better characterize the mechanism of disappearance of the Kondo effect. Neutron irradiated GC will be investigated to ascertain if the point defects introduced in this way have similar electrical properties and effects on structure as those that are annealed by heat treatment. Electrical measurements will be extended below 4.2 K to determine if the magnetoresistance effect approaches saturation at the highest fields and lowest. Some specimens heat treated at a higher temperature will be heat treated at a lower temperature to determine if the graphitization kinetics are altered by prior history.

Attempts will be made to use the Synchrotron Radiation Facility at SLAC to obtain precision wide range diffraction data from GC free of the large Compton component which obscures conventional data. This will permit an interpretation of structural parameters d_{002} , L_c and L_a by separating size and strain broadening. The kinetics studies of void growth will be completed. Initial studies of carbon fibers and intercalated highly oriented pyrolytic graphite will be initiated.

Plans are to complete the work on texture in the Al-CuAl₂ eutectic by Spring 1977, and begin the measurements of electrical, mechanical, and thermophysical properties of the series of alloys now at hand with lamellar spacings ranging from 1 to 10 μ .

9. 1976 PUBLICATIONS AND PRESENTATIONS

Robert H. Bragg and Associates

Journal

1. S. Justi and R. H. Bragg, Vickers Hardness of Unidirectionally Solidified Al-Si Eutectic Alloy

Grown at Different Rates, Met. Trans. A, 7A, 1954 (1976).

LBL Reports

1. R. R. Saxena, Structure and Electrical Properties of Glassy Carbon, (Ph.D. thesis), LBL-5129.
2. R. R. Saxena and R. H. Bragg, Negative Magnetoresistance in Glassy Carbon, LBL-5467.
3. R. R. Saxena and R. H. Bragg, Electrical Conduction in Glassy Carbon, LBL-5740.
4. R. R. Saxena and R. H. Bragg, Kinetics of Graphitization in Glassy Carbon, LBL-5799.

Papers Presented

1. K. Danso and R. H. Bragg, Electrical Resistivity Studies of Unidirectionally Solidified Al-CuAl₂ Eutectic Alloy, 105th AIME Annual Meeting, Las Vegas, February 1976.
2. D. F. Morrow and R. H. Bragg, Mechanical Properties of Directionally Solidified Al-Si Eutectic, 105th AIME Annual Meeting, Las Vegas, February 1976.

3. S. Bose and R. H. Bragg, Characterization of Oriented Voids in Pyrolytic Graphite," 2nd International Carbon Conference, Baden-Baden, West Germany, July 1976.

4. S. Bose and R. H. Bragg, Explanation of "Unorganized Carbon" in Glassy Carbon, 2nd International Carbon Conference, Baden-Baden, West Germany, July 1976.

5. R. R. Saxena and R. H. Bragg, Negative Magnetoresistance in Glassy Carbon, 2nd International Symposium on Amorphous Magnetism, RPI, Troy, New York, August 1976.

6. R. R. Saxena and R. H. Bragg, Electrical Properties of Glassy Carbon, 29th Pacific Coast Regional Meeting, American Ceramic Society, San Francisco, November 1976.

7. S. Bose, R. H. Bragg, and R. R. Saxena, X-ray Investigation of Glassy Carbon, 29th Pacific Coast Regional Meeting, American Ceramic Society, San Francisco, November 1976.

8. R. R. Saxena and R. H. Bragg, Graphitization Kinetics of Glassy Carbon, 29th Pacific Coast Regional Meeting, American Ceramic Society, San Francisco, November 1976.

B. SOLID STATE PHYSICS

1. EXPERIMENTAL RESEARCH

a. Far Infrared Spectroscopy

Paul L. Richards, Principal Investigator

1. INFRARED SURFACE SPECTROSCOPY

Robert B. Bailey and Paul L. Richards

A low temperature calorimetric technique for measuring infrared spectra is being developed which promises to increase the sensitivity of infrared spectroscopy in detecting molecules adsorbed on single crystal surfaces. Most of our knowledge of single crystal surfaces comes from studies employing beams of electrons or ultra-violet photons to probe the first few atomic layers of a solid sample. Infrared spectra can provide complementary information at lower energies and with very high resolution. However, the interaction cross sections are relatively small making conventional infrared transmission and reflection measurements difficult.

Our detection scheme uses techniques developed in constructing the composite far infrared bolometers discussed in article No. 2 following. A tiny doped germanium thermometer attached to the sample crystal measures the heat generated by the absorbed radiation. The time constant and minimum detectable absorbed power depend upon the heat capacity and temperature of the sample and upon the thermal conductance between the sample and its heat sink. Measurements are made at liquid helium temperatures where 10^{-15} watts of absorbed power can be detected with a one second integration time at modulation frequencies up to 500 Hz.

Infrared absorption by a single layer of atoms or molecules is less than 1% even for the most strongly interacting systems. By detecting this small absorption directly, rather than as a small change in the reflected or transmitted intensity, the requirements on the stability of a spectrometer are reduced and weaker absorptions may be observed. Our technique is most sensitive to surface effects when absorption by the clean substrate is small. For transparent crystals, absorptivities of a few parts per million can be measured.

A commercial (EOCOM) near infrared Fourier transform spectrometer has been interfaced to our computer system and modified for use as a signal source for this experiment. This spectrometer is capable of an ultimate resolution of 0.07 cm^{-1} throughout the chemical infrared and produces a typical output signal of $4 \mu\text{W}/\text{cm}^2$ in a throughput of 0.02 sterad cm^2 .

Figure 1 shows the absorption spectrum of a $4 \text{ mm} \times 8 \text{ mm} \times 0.1 \text{ mm}$ crystal of Al_2O_3 with a single layer of CO gas condensed on one face. The germanium thermometer is glued to the end of the sample and screened from the infrared radiation by

Fig. 1. Absorption spectrum for a monolayer of CO physically adsorbed on Al_2O_3 crystal.

(XBL 7611-7885)

optical baffles. The spectrum shows a strong CO vibrational mode and a weaker absorption from CO_2 present in the gas sample. Because the gases are physically adsorbed on the cold surface, their spectrum lacks the structure associated with molecular rotation or with chemical bonding to the Al_2O_3 . Background absorptions present before the gas was introduced, were subtracted away to produce this spectrum. Figure 2 is the difference between two spectra of the same crystal measured before and after rinsing it with reagent grade carbon tetrachloride. It indicates changes in the concentration of various organic impurities. Electrical noise from the germanium thermometer contributes structure on these spectra equivalent to fifteen parts per million fractional absorption and would permit detection of a strong absorber like CO for a surface coverage of only a few percent. Ten times greater sensitivity is anticipated when our system is optimized.

For highly reflecting metal substrates, sensitivity to surface absorption is maximum at grazing angles of incidence. Even for this geometry, the small background absorption by the free electrons of the bulk metal will always

Fig. 2. Difference spectrum showing changes in surface impurity concentration on an Al_2O_3 crystal. (XBL 7611-7884)

exceed that due to surface states. We are constructing an ultrahigh vacuum system in which clean surfaces can be prepared and analyzed under much more carefully controlled conditions. The difference between spectra of the same sample prepared with different surface properties will be used to isolate surface effects. In addition to detecting absorbed chemicals on catalytically active metals we hope to use this technique to identify surface electronic bands located within the energy gap of semiconductors and to study the optical properties of superconductors.

2. FAR INFRARED SEMICONDUCTING BOLOMETER DETECTORS

Norman S. Nishioka, Paul L. Richards, and David P. Woody

We are continuing our development of low temperature composite semiconducting bolometers for the detection of far infrared radiation. The construction of these bolometers is shown in Fig. 1 and in the 1975 MMRD Annual Report. These detectors are now used for far-infrared detection in our laboratory on a routine basis. In addition, a detector of this type has been flown in our high altitude balloon experiment to measure the spectrum of the cosmic background radiation described in article No. 7 following. The most sensitive bolometer of this type yet constructed has an area of $4 \times 4 \text{ mm}^2$, a time constant of 25 ms, and an NEP of $3 \times 10^{-14} \text{ W}/\sqrt{\text{Hz}}$ at a bath temperature of 1.2 K.

COMPOSITE Ge BOLOMETER

Fig. 1. The composite semiconducting bolometer. A $200 \Omega/\square$ Bi film on a thin sapphire substrate absorbs incident far infrared radiation. The temperature is measured with a Ga:Ge thermometer. Mechanical support is provided by nylon threads and thermal contact to the heat sink by the electrical leads to the thermometer. (XBL 7611-7706)

Although the superconducting transition edge bolometer discussed in article No. 3 is more sensitive by a factor of ~ 10 , semiconducting bolometers remain useful for several reasons: (1) The electronic system, that consists of a low noise preamplifier and a bias supply is straightforward to construct and operate; (2) The dynamic range is large ($\sim 10^7$); (3) The bolometer will operate over a wide range of bath temperatures; (4) It is unconditionally thermally stable so that thermal runaway is impossible; (5) It can be operated in the presence of high magnetic fields.

The design of these bolometers has been guided by computer simulations of their performance. These calculations indicate a complicated relation between the optimum bolometer parameters and the optical environment under which the bolometer is to be used. In addition, they indicate that a significant improvement in sensitivity can be obtained by using liquid ^3He instead of liquid ^4He as the coolant. We have recently completed the construction and testing of a charcoal pumped liquid ^3He cryogenic system that operates at a temperature of 0.3 K. The construction and testing of semiconducting bolometers for use at these temperatures is also in progress. If the anticipated improvement in sensitivity is achieved, these detectors will become the most sensitive detectors of far infrared radiation.

3. FAR INFRARED SUPERCONDUCTING BOLOMETER DETECTORS

John Clarke, Paul L. Richards, and N.-H. Yeh

We have continued the development of composite far infrared bolometer detectors with superconduc-

ting thermometers. These are the most sensitive far infrared detectors yet made. With an area of 2×4 mm, a time constant of 50 ms, and an operating temperature of 1.4 K, the electrical NEP has been measured to be 1.5×10^{-15} W/Hz. This sensitivity is limited by fundamental thermodynamic fluctuations which depend only on the temperature and the thermal contact to the heat sink.

A new electronic system has been developed in an attempt to make these detectors easier to use in practical applications. This electronic system includes a 1 KHz oscillator for AC bias, a helium temperature bridge circuit and step-up transformer, a lock-in detector, and current feedback to stabilize the temperature of the bolometer on the superconducting transition. The convenience of operation of this integrated electronic system is such that we can now contemplate using bolometers of this type in the White Mountain radiometer and the far infrared sky survey discussed in article Nos. 8 and 9 following.

The absorbing element used in these bolometers is a $200 \Omega/\square$ bismuth film evaporated on the back side of sapphire substrate. Measurements of the transmittance of such combinations showed that the absorptivity in large area samples was ~50%. Detailed modeling experiments are being carried out to determine how best to optimize the absorptivity of composite bolometer structures.

SUPERCONDUCTING TRANSITION EDGE BOLOMETER

Fig. 1. The composite superconducting bolometer. Nylon threads coated with In and welded to In tabs on the substrate provide mechanical support and thermal contact for the substrate as well as electrical contact to the Al film thermometer and to the Bi film heater which is used for calibration. (XBL 7611-7707)

4. OPTO-ACOUSTIC FOURIER SPECTROSCOPY

Gary T. Boyd and Paul L. Richards

Opto-acoustic spectroscopy is a technique in which absorbed electromagnetic energy in a gas causes a rise in gas pressure which is detected in a sensitive microphone. This technique is currently being used as a detection system with infrared lasers, and with conventional spectrometers in the visible and ultraviolet. It has

also been used in a commercial infrared gas analyzer. We are exploring the use of opto-acoustic spectroscopy as a detection technique in the chemical region of the infrared, using a Fourier transform spectrometer as a signal source. In this approach, the intensity variations of the interferogram are used to thermally excite a gas sample whose resulting pressure fluctuations are detected with a microphone and Fourier transformed to extract the infrared spectrum of the gas.

In order to evaluate the performance of this technique, we have compared the spectra obtained from a 5 cm long opto-acoustic cell with those obtained by transmission through the cell and detection with a good quality commercial pyro-electric detector. In both experiments the cell is filled with CO gas at about half atmospheric pressure. The random noise level in the opto-acoustic spectrum shown in Fig. 1 is about ten times larger than that of the spectrum obtained using the pyro-electric detector. This is a very promising result because the opto-acoustic cell has not been optimized. By contrast, many man-years of effort have gone into optimization of the pyro-electric detector.

Fig. 1. Comparison of signals from the opto-acoustic detector (left) and the pyro-electric detector (right). (XBL 7611-7883)

The opto-acoustic spectrum shown at the left in Fig. 1 was obtained by subtracting the amplitude Fourier transform of the interferogram obtained with an empty cell from that of the full cell. The spectrum is dominated by the CO vibrational lines at $\sim 2150 \text{ cm}^{-1}$. The scan rate of the interferometer was such that the audio frequency of operation was ~ 450 Hz. This frequency was much higher than the relaxation frequency of the cell. The microphone amplifier was the dominant source of random noise. Small spikes associated with harmonics of 60 Hz pickup are apparent. These can be eliminated by suitable shielding.

The signal from the opto-acoustic cell could be enhanced by reducing the operating frequency, and by decreasing the dead space in the cell. It seems possible that with optimum cell design, the signal-to-noise ratio in the opto-acoustic detector could be comparable to that in the pyro-electric detector.

The curve on the right in Fig. 1 is the difference between the amplitude transformed spectrum of the empty and filled cells, normalized to that of the empty cell. A characteristic feature of this form of spectroscopy is the base-line drift and the residual absorption from uncompensated atmospheric CO₂ which appears as a negative feature. Although these effects can be reduced by suitable attention to technique, the base-line is rarely as flat as in the opto-acoustic technique.

5. FAR-INFRARED SPECTROSCOPY OF ELECTRONS ON THE SURFACE OF LIQUID HELIUM

David K. Lambert and Paul L. Richards

Electrons attracted to a liquid helium surface by the combination of an image field and an applied electric field populate surface states in which the charge is highly mobile in the plane of the surface, but cannot escape from it. Transitions between bound states of the system have been observed by others at microwave frequencies for external field strengths ≤ 200 volts/cm. At higher fields many body effects begin to play a role, but the absorption frequencies are stark-shifted from microwave frequencies into the far infrared.

This project has the object of measuring the properties of this system in the unexplored high-field, high density region. Among the interesting properties which have been theoretically predicted, but not experimentally observed are: (1) The condensation of the electrons into a two-dimensional Wigner lattice; (2) Nonlinear interaction of the electronic transitions with fluid and plasma waves; (3) A Rayleigh-Taylor instability in which the electrons sink into the liquid.

A cryogenic system has been constructed which will permit electric field confinement of electrons on a free liquid helium surface. The confinement will be accomplished inside a far infrared transmittance cavity. Care is being taken to isolate vibrations which would cause ripples on the helium surface.

Two far infrared signal sources are being prepared for this experiment. A far infrared polarizing interferometer that was constructed last year has been optimized for high efficiency and spectral fidelity in the frequency range from 2 to 70 cm⁻¹. This is a general purpose laboratory tool which is now in use for a number of applications. The polarizing interferometer is now being used to evaluate cavity designs for this experiment. A CO₂ pumped molecular laser which was constructed last year is being optimized for

high CW power output and high stability. The first experimental attempts to see transition between the bound state of electrons trapped on the surface of liquid helium will be made using the molecular laser source.

6. JOSEPHSON EFFECT MILLIMETER WAVE RECEIVERS*

John H. Claassen, Paul L. Richards, Tek-Ming Shen, and Yuan Taur

We are evaluating the usefulness of superconducting Josephson junctions as low noise receivers of coherent millimeter wave radiation. Results of this program to date include: (1) the construction of a millimeter wave heterodyne mixer with the lowest noise yet achieved ($T_m = 54$ K at 36 GHz); (2) preliminary evaluation of a similar mixer at 140 GHz; (3) operation of a Josephson junction parametric amplifier at 36 GHz with a gain of 12 dB and a noise temperature of less than 50 K. In each of these devices the active element is a single point contact Josephson junction.

Theoretical calculations of the expected performance of each of these devices have been carried out using digital and analog computers and the resistively shunted junction model of a Josephson point contact. Detailed comparisons have been made between the conclusions from these calculations and the experimental observations. Good agreement is found in most cases which allows us to set theoretical limits to the performance of optimized devices.

Current activities are centered around analog computer calculations of the effect of the coupling circuit on a Josephson effect mixer. We are also investigating the use of a high speed superconducting transition edge bolometer as a heterodyne mixer. Attempts to make heterodyne mixers from series arrays of Josephson effect thin film bridges have not been successful because the bridge quality is not adequate for this purpose.

*This program is totally supported by the Office of Naval Research.

7. MEASUREMENT OF THE SPECTRUM OF THE SUBMILLIMETER COSMIC BACKGROUND*

Norman S. Nishioka, Paul L. Richards and David P. Woody

The observed spectrum of the cosmic background radiation (CBR) is in agreement with the blackbody spectrum which is predicted by elementary "Big Bang" cosmology over the frequency range from 0.013 to 17 cm⁻¹. The temperature is 2.9 K. The spectrum in the frequency range from 4 to 17 cm⁻¹ was established during the July 24, 1974 flight of our liquid helium cooled spectrophotometer. This frequency range includes the peak in the 2.9 K blackbody spectrum at 6 cm⁻¹ and the Planck high

frequency cutoff. We are presently improving our measurements of the submillimeter CBR to look for possible deviations from the Planck curve. Any such deviation should be most visible in the submillimeter part of the spectrum.

The liquid helium cooled spectrophotometer has been modified to both increase its sensitivity and reduce possible systematic errors. The sensitivity has been increased by a factor of five by installing one of the composite bolometers described in preceding article No. 2.

The atmospheric line emission and continuum emission from the earth and the apparatus itself are possible sources of systematic errors. The improved sensitivity allows us to obtain higher resolution ($\Delta\nu \approx 0.1 \text{ cm}^{-1}$) spectra and thus more accurately measure the atmospheric line emission. The resolution and sensitivity are such that a meaningful check on the accuracy of our atmospheric model, including the emission line parameters for H_2O , O_3 , and O_2 in the submillimeter frequency range, can now be made. Figure 1 is a calculated spectrum of the emission of the night sky at our presently achievable resolution and altitude. The continuum contributions to the observed spectrum have been decreased by incorporating a Winston light condenser and a flared horn into the radiation collecting antenna.

Fig. 1. Calculated night sky emission at an altitude of 43 km. The emission from a 3 K blackbody is shown as a dashed line. (XBL 7611-7834)

This modified instrument was flown from Palestine, Texas on April 21, 1976. The apparatus performed satisfactorily except for a loss in responsivity. As a result, no improvement was obtained over the results from the July 24, 1974 flight. A series of tests is under way to identify and correct the cause of this failure.

The recent progress we have made in developing ^3He temperature composite bolometers should allow us to increase the sensitivity by another order of magnitude. A self-contained ^3He cryostat has been successfully operated at a temperature of 0.3 K and semiconductor chips suitable for construction of 0.3 K bolometers are being tested.

A flight of the spectrophotometer incorporating a new ^3He temperature bolometer is planned for the Spring of 1977.

* This program is being carried out in collaboration with the Berkeley Space Sciences Laboratory and has received support from NASA.

8. WHITE MOUNTAIN RADIOMETER

James L. Bonomo, David D. Cudaback, Mark R. Hueschen, Andrew D. Jeffries, Paul L. Richards, and David P. Woody

Our development of improved far infrared bolometer detectors discussed in preceding articles Nos. 2 and 3, and the availability of a new infrared telescope, has created a scientific opportunity for ground based far infrared astronomy. The new 62" diameter infrared telescope is a joint venture between the University of California at Berkeley and Caltech. It has been located at an altitude of 13,000 feet on White Mountain, east of Bishop, California.

A collaboration has developed between members of the Astronomy Department at Berkeley and the MMRD to exploit the opportunities raised by these developments. A new far infrared radiometer has been built that makes use of low background composite bolometers and an optical scheme similar to that developed for the sky survey. The techniques of photolithography have been used to produce a set of metal mesh filters which isolate frequency bands in which the atmosphere is relatively transparent. The radiometer is designed to mount in the center of the f/1 primary mirror of the telescope. A hyperbolic secondary mirror has been developed which wobbles so as to modulate the intensity reaching the detector from localized sources such as stars galaxies and interstellar dust clouds.

The construction of these instruments is well advanced and an observing program is expected to begin in the Winter of 1976-77.

Data from this project should not only answer important astronomical questions, but also should be extremely useful in checking new sources of far infrared radiation discovered by the sky survey discussed in article No. 9 following.

9. FAR INFRARED SKY SURVEY*

Stephen E. McBride, Norman S. Nishioka, Paul L. Richards, and David P. Woody

Astronomy in the far infrared has always been limited by the lack of sensitive detectors. Our development of new bolometers with greatly improved sensitivity now makes it possible to do much exciting astronomy. We are preparing to survey the sky in an unbiased way to see what sources can be found at far infrared wavelengths.

Fig. 1. Schematic diagram of the sky survey telescope. (XBL 7510-7473)

We are constructing the one-meter Cassegrain balloon telescope, shown in Fig. 1. Since any radiation from warm objects reaching the detectors would limit their sensitivity, great care has gone into the design of this telescope to insure that it accepts the minimum feasible thermal background radiation. This includes a cold stop near the top of dewar to limit thermal radiation being diffracted into the detectors, diamond machined metal optics (developed at the Lawrence Livermore Laboratory for the laser fusion program) for the lowest emissivity reflecting surfaces, cold Winston light concentrators (developed at the Argonne National Laboratory) to define the entrance beam into the cryostat, and careful shielding to minimize background radiation originating from the gondola and from the earth. There are seven bolometer detectors, each responding to a separate frequency band between 10 cm^{-1} and 1000 cm^{-1} . These frequency bands are isolated by cold filters in the optical path. Winston light concentrators are used both to define the beam and to efficiently concentrate the radiation as is shown in Fig. 2.

Fig. 2. Schematic diagram of bolometer feed system. The Winston concentrator A is used to define the input solid angle Ω_i , B is used to collimate the beam for effective filtering, and C is used to concentrate the beam onto the bolometer. (XBL 7611-7708A)

The angular field of view of the telescope will be 11 arc minutes, the 2 rpm rotation rate of the telescope was chosen so that each portion of the sky will be observed a minimum of four times during the survey. The survey will be sensitive to extended sources, several degrees across. Accurate orientation information will be obtained from a photomultiplier with an N shaped mask, that will detect the optical signals from the transit of stars with known positions.

With the present apparatus floating at an altitude of $\sim 30\text{ km}$, the limiting flux sensitivity should be a few flux units ($1\text{ f.u.} = 10^{-26}\text{ W/m}^2\text{ Hz}$) in the far infrared bands. This is orders of magnitude more sensitive than previous surveys. The apparatus is presently in the final stages of construction and testing, and should make its first flight in early 1977.

* This project is partially supported by a grant from the Director of the LBL.

10. RESEARCH PLANS FOR CALENDAR YEAR 1977

Paul L. Richards

Surface Physics. Exploration of the usefulness of thermal detection techniques for the measurement of the spectra of molecules adsorbed onto solid surfaces will continue. An ultra-high vacuum system will be constructed so that these experiments can be carried out on clean single crystal surfaces.

Bolometer Development. Composite bolometers with semiconducting thermometers will be developed for operation at ^4He temperatures. The development of the superconducting transition edge bolometer will be continued so that it can be used in practical laboratory measurements. The experimental investigation of the efficiency of the coupling of composite bolometers to focus free-space electric magnetic waves will be continued.

Opto-Acoustic Spectroscopy. Calculations and optimization experiments will be carried out to determine the fundamental noise limits of opto-acoustic cells designed for use with infrared Fourier spectrometers.

Electrons on the Surface of Liquid Helium. The development of apparatus for this project will be continued, and the first measurements are expected.

Infrared Astrophysics. The improved cosmic background experiment will be flown to search for deviations from the blackbody spectrum. The sky survey telescope will be flown for the first time. The new radiometer will be used on White Mountain for far infrared astronomical measurements.

Semiconductor Physics. A new project will be initiated to measure the shallow impurity energy levels in ultra-pure germanium. Fourier transform spectroscopy will be used to measure the photo-

thermal spectra of the impurity levels in the presence of very large uniaxial stress. Calculations of impurity energy levels had been complicated in the past by degeneracies in the valence and conduction bands. Data on the impurity energy levels obtained in large uniaxial stress can be compared with simpler nondegenerate theories.

11. 1976 PUBLICATIONS AND REPORTS

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† Sponsored by the Advance Research Projects Agency.

b. Experimental Solid State Physics and Quantum Electronics

Y. Ron Shen, Principal Investigator

1. MOLECULAR BEAM STUDIES OF MULTIPHOTON DISSOCIATION OF POLYATOMIC MOLECULES*

Michael J. Coggiola, Edward R. Grant, Peter A. Schulz, Yuan T. Lee, and Y. Ron Shen

The discovery of multiphoton dissociation of polyatomic molecules in an intense laser field is one of the most exciting developments in recent years.¹ The potential applicability of this method in promoting selective chemical reactions for chemical synthesis, in separation of isotopes, and in many other branches of chemistry has led to an intensive effort towards an understanding of the dissociation process. In spite of numerous detailed experimental studies and the recently improved theoretical understanding of the nature of multiphoton absorption, many important questions have remained unanswered. For example, in the multiphoton dissociation of SF_6 molecules, the fragments have not yet been positively identified, although it was believed that the major products

could be either $\text{SF}_5 + \text{F}$ or $\text{SF}_4 + \text{F}_2$ or others depending on the laser intensity. It is also not sure how many photons a single molecule can absorb beyond the dissociation limit, and how the excess energy is distributed among the fragments. Furthermore, little is known about the dynamics of multiphoton molecular dissociation, the existence of an activation barrier in the exit channel beyond the dissociation limit and the effect of molecular collisions. These questions and many others, however, can be answered by studying multiphoton dissociation with a molecular beam machine. We have recently carried out such an experimental study on SF_6 with crossed CO_2 laser and molecular beams. We have identified the primary dissociative products to be $\text{SF}_5 + \text{F}$. For laser pulses ~ 500 nsec long, secondary dissociative products from dissociation of SF_5 into $\text{SF}_4 + \text{F}$ have also been seen. We have measured angular and velocity distributions of the fragments. Figure 1 is an example of the angular distribution of the SF_5 fragment. The results indicate that no more than 7 infrared photons can be absorbed in excess of the dissociation threshold and the activation barrier for dissociation is negligibly small.

Fig. 1. (a) Angular distribution of the fragment products. (b) Kinematic diagram for fragments of SF_6 . The circles show the total amount of translational energy released (in kcal), when the SF_5 is found in the phase space which lies on the circle. (XBL 769-10330)

* This project is in collaboration with Prof. Yuan T. Lee's group.

1. See, for example, papers on the subject presented at the Laser Chemistry Conference, Steamboat Springs, Colorado, (February, 1976) and at the Nordfjord Conference on Tunable Lasers and Applications (June, 1976), and references therein.

2. NONLINEAR EXCITATION AND DETECTION OF SURFACE POLARITON WAVES

Francesco DeMartini and Y. Ron Shen

Stimulated by the recent development in surface physics, there has been rapidly growing activity in the field of surface polaritons and plasmons. A large number of reports on the subject exist in the literature dealing with experimental investigation using various methods: inelastic electron diffraction, attenuated total reflection, grating coupling, spontaneous Raman scattering, etc. Studies of surface polaritons and plasmas can lead to information about oxide or molecular overlayers on semiconductor and metal surfaces. We have shown theoretically¹ that surface polaritons and plasmons can be excited and detected also by nonlinear optical mixing of two laser beams. We have now succeeded in demonstrating experimentally the feasibility of the method in our laboratory. We used the four-wave mixing scheme to coherently excite and detect the surface polaritons in GaP and to measure their dispersion characteristics.

Fig. 1. Experimental setup. The inset shows the wavevector diagram for the four-wave mixing process. (XBL 764-6740)

Our experimental setup of four-wave mixing is shown in Fig. 1. A Q-switched ruby laser with a

Fig. 2. Experimental results of normalized $I(\omega_4, \Delta k_X)$ vs. Δk_X at $\omega = 370, 380, 390$, and 395 cm^{-1} , where $\Delta k_X = k_{1X} - k_{2X}$. The solid curves are Lorentzian used to fit the data points. (XBL 764-6741)

30-psec pulsewidth provided a beam at $\omega_1 = 14403 \text{ cm}^{-1}$. It was also used to pump simultaneously two dye lasers emitting two tunable laser beams at ω_2 and ω_3 with a linewidth of $\sim 1.5 \text{ cm}^{-1}$. In the experiment, ω_3 was held fixed at 13333 cm^{-1} while ω_2 was tuned in the range between 14006 and 14035 cm^{-1} so that optical mixing of ω_1 and ω_2 beams could excite surface polaritons in the range between 368 and 397 cm^{-1} . For each given

$\omega = \omega_1 - \omega_2$, we measured $I(\omega_4)$ as a function of k_X around $\Delta k_X = 0$. The value of k_X was adjusted by varying the $\vec{k}_1$ direction and hence varying the angle θ between $\vec{k}_1$ and $\vec{k}_2$. Some examples are shown in Fig. 2. It shows that at each ω , the experimental results $I(\omega_4, \Delta k_X)$ vs. Δk_X where $\Delta k_X = k_{1X} - k_{2X}$ can be fit by a Lorentzian curve. The theory predicts that the peak of the curve occurs at the wavevector $K_X'(\omega)$ determined by the surface polariton dispersion while the width of the curve gives the surface polariton damping coefficient $K_X''(\omega)$. Thus, in Fig. 3, we have plotted the data points deduced from the experimental results and the theoretical curves of $K_X'(\omega)$ and $K_X''(\omega)$ calculated from the dispersion relation for surface polaritons.

Fig. 3. Measured dispersion characteristics of surface polaritons in GaP. (O — K_X' vs. ω ; Δ — $2K_X''$ vs. ω .) The solid curves are calculated from the single-oscillator model. (XBL 764-6739)

$$(K_X' + i K_X'')^2 = (\omega/c)^2 \epsilon/(1 + \epsilon)$$

where $\epsilon(\omega) = \epsilon_\infty + \omega_p^2 / [\omega_T^2 - \omega^2 - i\omega_T\Gamma]$, with $\epsilon_\infty = 9.091$, $\omega_T = 367.3 \text{ cm}^{-1}$, $\omega_p^2 = 1.859 \omega_T^2$, and $\Gamma = 1.28 \text{ cm}^{-1}$. The agreement between theory and experiment for K_X' is good. The agreement for K_X'' is satisfactory at larger ω , but the experimental K_X'' approaches a constant and deviate from the theoretical curve as ω decreases towards ω_T . This is because we focused beams in the experiment so that at small K_X'' , the observed width of the $I(\omega_4)$ curve was dominated by the spread of k of the focused beam.

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3. OPTICAL SUM-FREQUENCY GENERATION IN METAL VAPOR VIA QUADRUPOLE TRANSITIONS

Don S. Bethune, Robert W. Smith, and Y. Ron Shen

Nonlinear optical effects in atomic vapor have recently been studied quite extensively. Because of their large resonant nonlinear susceptibilities, wide ranges of transparency, and high optical breakdown thresholds, atomic vapors are excellent nonlinear media for generation of new coherent radiation. Thus, in atomic vapors, third-harmonic generation has been used to generate soft x-ray and vacuum UV radiation, four-wave mixing processes to generate tunable vacuum UV and infrared, and stimulated Raman scattering to generate tunable infrared. Nevertheless, in all cases reported to date, third-order and occasionally odd high-order nonlinearities of the vapors are always responsible for the observed effects. The second-order nonlinear processes, being forbidden by symmetry under electric-dipole approximation, were believed to be too weak to be significant. We however realize that in many cases, if electric-quadrupole transition matrix elements are taken into account in nonlinear susceptibilities, then an n -th-order electric dipole-forbidden process can often be as strong as or stronger than an $(n+1)$ -th-order allowed process. Hänsch and Toschek¹ have considered collinear sum-frequency generation (SFG) due to dipole forbidden susceptibilities, and concluded that it will not occur. We have however succeeded in showing both theoretically and experimentally that noncollinear second-order SFG in atomic vapors is in fact easily observable. The effect may be used to generate coherent tunable UV radiation over certain narrow ranges.

We consider the case of sodium with two pump laser frequencies ω_1 and ω_2 close to the $3s \rightarrow 3p$ transitions respectively. Under electric-dipole approximation, the second-order nonlinear susceptibility $\chi^{(2)}$ should vanish. But if we include the electric-quadrupole matrix element between $4d$ and $3s$, then we can have $\chi^{(2)} = 1.6 \times 10^{-24} N \text{ esu}$, where N is the density of atoms. This magnitude of $\chi^{(2)}$ shows that the sum-frequency generation should be easily observable.

When $\omega_1 + \omega_2 \approx \omega_{4d}$, and the angle θ between the two pump laser beams was adjusted close to the phase-matching angle θ_p , we could in fact easily detect a coherent sum-frequency UV beam at $\sim 34549 \text{ cm}^{-1}$, even if the laser powers were as small as 1W. The sum-frequency output was always polarized along $\vec{k}_1 \times \vec{k}_2$ in agreement with the predicted selection rule.

With ω_1 fixed and ω_2 varied over a narrow range, the sum-frequency output should have a sharp resonance at $\omega_1 + \omega_2 = \omega_{4d}$. We show in Fig. 1(a) such a resonant curve. In this case, the width of the curve was dominated by the laser spectral widths. A typical phase-matching curve, obtained by varying the angle θ and keeping the other variables fixed, is shown in Fig. 1(b), together

Fig. 1(a). Sum-frequency output $P(\omega_3)$ as a function of ω_2 showing the sharp resonance at $\omega_1 + \omega_2 = \omega_{4d} = 34548.8 \text{ cm}^{-1}$. $P_1 = 2 \text{ W}$; $P_2 = 25 \text{ W}$; $\theta = 47.9 \text{ mrad}$; $N = 1.6 \times 10^{16} \text{ cm}^{-3}$.

(b) Phase-matching curve $P(\omega_3)$ vs. θ . $P_1 = 2 \text{ W}$; $P_2 = 25 \text{ W}$; $\omega_1 - \omega_{3p/2} = -25.6 \text{ cm}^{-1}$; $\omega_1 + \omega_2 = \omega_{4d}$; $N = 1.6 \times 10^{16} \text{ cm}^{-3}$. The dashed curve is a theoretical curve. (XBL 766-7039)

with the theoretical phase-matching curve. Other experimental results as functions of N and ω_1 also agree well with theoretical predictions.

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Eric G. Hanson and Y. Ron Shen

A line graph showing the relationship between the reduced minimum radius, $R_{\min}$, and the normalized input peak power, P/P_{cr} . The y-axis, labeled 'REDUCED MINIMUM RADIUS, $R_{\min}$ ', ranges from 0.1 to 1.0. The x-axis, labeled 'NORMALIZED INPUT PEAK POWER, P/P_{cr} ', ranges from 0 to 40. Eight curves, labeled (a) through (h), originate from the point (0, 1.0). Curve (a) is a vertical dashed line at $P/P_{cr} \approx 1.5$. Curve (b) is a solid line with open circles, decreasing to $R_{\min} \approx 0.15$ at $P/P_{cr} \approx 10$. Curve (c) is a solid line with open circles, decreasing to $R_{\min} \approx 0.1$ at $P/P_{cr} \approx 10$. Curve (d) is a solid line with open triangles, decreasing to $R_{\min} \approx 0.1$ at $P/P_{cr} \approx 10$. Curve (e) is a solid line with open squares, decreasing to $R_{\min} \approx 0.1$ at $P/P_{cr} \approx 10$. Curve (f) is a solid line with open circles, decreasing to $R_{\min} \approx 0.1$ at $P/P_{cr} \approx 10$. Curve (g) is a dashed line, decreasing to $R_{\min} \approx 0.1$ at $P/P_{cr} \approx 10$. Curve (h) is a dashed line, decreasing to $R_{\min} \approx 0.1$ at $P/P_{cr} \approx 10$. Arrows point to curves (b) and (f) at $P/P_{cr} \approx 15$.

(XBL 766-7031)

* Partially supported by NSF.

James R. Morris and Y. Ron Shen

We have found that focusing of the pump beams can greatly enhance the far infrared output. In a crystal of 1 cm long, the optimum focal spot radius is roughly equal to or smaller than the far infrared wavelength for output frequencies less than 100 cm^{-1} . The walkoff effect of the pump beams in birefringent crystals does not reduce the output by more than a factor of 2. Far infrared absorption and boundary reflections are however extremely important. The former is often the factor which limits the output power.

We show that the usual plane-wave model which neglects the effects of far infrared diffraction and boundary reflections does not give a correct description of the far infrared output, especially for tightly focused pump beams. A simple model treating the nonlinear polarization as a constant

$1/e$ radius Gaussian distribution of radiating dipoles is, however, a good approximation to the real picture. We also compare our results with those of second-harmonic generation and notice many similarities. Most of the differences can be ascribed to boundary effects, including total reflection, which are more important in the case of far infrared generation.

6. STUDY OF HOMOLOGOUS NEMATIC MATERIALS BY REFRACTIVE INDEX MEASUREMENTS*

Eric G. Hanson and Y. Ron Shen

Among the many interesting properties of liquid crystals, optical birefringence is probably the most important. It is the basis of liquid crystal display as well as other device applications. Physically, the strong optical birefringence arises from alignment of molecules with large molecular anisotropy. The molecular anisotropy reflects not only the geometric shape of the molecules but also anisotropy of their electronic orbitals. With increasing molecular alignment in the nematic phase, the optical birefringence increases accordingly. It can therefore be used as a measure of the nematic order. These measurements carried out on a homologous series of liquid crystals could yield valuable information about the effects of molecular structure on refractive indices, optical anisotropy, and molecular ordering. No such measurements have yet been reported.

We have measured as functions of temperature the refractive indices and linear birefringence of seven homologous compounds of p, p'-di-n-alkoxy-azoxybenzenes ($C_nH_{2N+1}O-C_6H_4-N_2O-C_6H_4-OC_nH_{2N+1}$ with $N = 1, \dots, 7$). Using the Vuks' model of local-field correction and calibrating the microscopic parameter at one temperature against that obtained by Pines et al. from NMR measurements,¹ we have deduced as functions of temperature absolute values of both microscopic (S) and macroscopic (Q) order parameters for these compounds, as shown in Fig. 1. The former agrees very well with the results of Pines et al. Our results also indicate that the use of the linear birefringence $\delta n(T)$ as a direct measure of the temperature dependence of the order parameter could lead to a few percent error.

We have shown that for all the homologous compounds, the microscopic order parameter S as a function of temperature can be described by a simple equation $S = S_0(1 - T/T^*)^Y$, but S_0 is not equal to 1 as has been suggested by others. Our results on the homologous series also yield information about the effects of molecular structure on the optical properties. We have found that with increasing N from 1 to 7 in the C_nH_{2N+1} alkyl chain the average polarizability increases by a factor of 1.8 while the polarizability anisotropy only increases by a factor of 1.18. Using Marčelja's calculation,² we have also been able to deduce separately the contributions to the polarizability anisotropy from the core and from the CH_2 groups in the chain.

Fig. 1. (a) Comparison of microscopic order parameters obtained in this work for p-azoxyanisole (PAA) with those of Pines et al. (b) Comparison of Q vs. T with δn vs. T for PAA. (XBL 762-6476)

* Partially supported by NSF

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7. OPTICAL STUDY OF SURFACE ACOUSTIC WAVE PROPAGATION ON WATER AND NEMATIC FILMS*

Ken Miyano and Y. Ron Shen

Acoustic wave propagation in layered media has been studied quite extensively. In particular, sound propagation in fluid sandwiched between two solid plates has attracted much attention because of its applications in delay line and in coupling of surface waves between separate surfaces. Two kinds of modes exist in the fluid film: the waveguide modes and the surface-like modes. So far, only the group velocities of the waveguide modes have been measured. The phase velocity, however, is a more fundamental quantity. Using optical diffraction, we have measured the phase velocities of various ultrasonic modes in water films of different thicknesses sandwiched between two glass plates. The results agree very well with theory as shown in Fig. 1.

We have also studied the propagation of ultrasonic waves in homeotropic nematic films sandwiched between glass plates. With the sandwiched film between crossed polarizers, we observed a semiperiodic stripe pattern. We found that flow reorientation of molecules in the nematic film was responsible for the observed pattern while

Fig. 1. Thickness dependence of the phase velocities of various acoustic modes in water films between glass plate. WE: even waveguide modes, WO: odd waveguide modes, and SE: even surface-like mode. Dots are experimental data and solid curves are from theoretical calculation. (XBL 762-6528)

(a)

(b)

Fig. 2. (a) Photograph of the domain pattern induced in a homeotropic nematic (MBBA) film of 44 μm thick. Sound propagated from left to right. The sample was between crossed polaroids with axes at 45° with respect to the stripes. (b) Calculated transmission coefficient as a function of distance. (XBL 765-4086)

acoustic streaming resulting from nonlinear mixing of the propagating acoustic modes in the film was cause of the fluid flow. A complete theory has been developed to describe the effect of sound-induced flow reorientation. As shown in Fig. 2, the theory explains very well the observed stripe pattern.

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8. MODULATION SPECTROSCOPY OF SEMICONDUCTING GROUP IV-A AND IV-B DICHALCOGENIDES

Jean Camassel, Stanley Kohn, and Y. Ron Shen

The group IV-A and IV-B dichalcogenides are semiconductors crystallized in the CdI_2 layer structure. It consists of a plane of metal atoms sandwiched between two planes of chalcogens. In the layer, the coordination of a metal atom respective to the 6 neighboring chalcogens is octahedral. We used in our experiment crystals of SnS_2 , SnSe_2 , and HfS_2 grown by an iodine transport method. The crystals were in the form of platelets with the $\hat{c}$ -axis perpendicular to the large surfaces. Our optical measurements were restricted to the $\hat{E} \perp \hat{c}$ geometry.

We have measured both the normal reflectivity R and wavelength derivative reflectivity $1/R \cdot dR/dE$ of HfS_2 , SnS_2 , and SnSe_2 at 5°K and 300°K , in the range 2 eV - 6 eV. The results are shown in Fig. 1. We also did piezotransmission measurements, in order to help resolve the fine structure of their indirect absorption edges. On the basis of existing band structure calculations, we have made the assignment to the observed structures in Tables 1, 2, and 3.

Fig. 1. Reflectivity (R) and derivative reflectivity ($1/R \cdot dR/dE$) of (a) SnS_2 ; (b) SnSe_2 ; (c) HfS_2 at 300°K and 5°K . (XBL 773-590)

Table 1. Listing of interband transitions of SnS_2 .

Previous Works		This Work		Assignment
(300 K)		(300 K)	(5 K)	
(a)	(b)			
2.21	2.07		2.255 ^(c)	$\Gamma_{2-} \rightarrow M_1^+$
		2.32	2.50	
			2.61; 2.70	
	2.88	2.82	2.81; 2.90; 2.95	M, L ($8 \rightarrow 9$)
		3.32	3.37	
3.8		3.57	3.61; 3.80; 3.92	Σ ($8 \rightarrow 9$)
		4.37	4.17; 4.53	T ($8 \rightarrow 9$)
4.9		4.89	4.98	K ($8 \rightarrow 9$)
		5.90; 5.41	5.22; 5.32	H ($7 \rightarrow 9$)
5.8		5.74	5.58; 5.85	S ($6 \rightarrow 9$)
5.9		6.04		
6.6				
<hr/>				
(a) Ref. 1				
(b) Ref. 2				
(c) Piezotransmission (80 K)				

Table 2. Listing of interband transitions for SnSe_2 .

Previous work			This work		Assignment
300 K	77 K		300 K	5 K	
(a)	(b)	(c)			
0.97	1.03			1.105 ^(d)	
	1.30			1.30 ^(d)	
1.62	1.97	1.7; 1.8; 2.0;	1.92	1.92	
		2.3			
		2.8; 3.2	2.88	3.05	
		3.6	3.52	3.60; 3.66	
				3.75	Σ ($8 \rightarrow 9$)
		3.9	3.79	3.88; 3.91; 3.95	Γ , K ($8 \rightarrow 9$)
				3.99; 4.05	R, U ($6 \rightarrow 9$)
			4.09	4.19; 4.30	R, U ($6 \rightarrow 9$)
		4.5	4.27; 4.46	4.45; 4.55	Γ ($7 \rightarrow 9$)
		4.9	4.76; 5.06	4.91; 5.06	M ($8 \rightarrow 10$)
		6	5.58	5.29; 5.71	
		7.1			
		9.6			
<hr/>					
(a) Ref. 2			(c) Ref. 4		
(b) Ref. 3			(d) Piezotransmission (77 K)		

Table 3. Listing of interband transitions for Hf S₂.

300 K	5 K	300 K	5 K	Theoretical Assignment (from Ref. 5)
(a)	(b)			
1.96			1.75 ^(c) 2.10 ^(c)	$\Gamma_2^- \rightarrow M_1^+$
2.9	2.88	2.81	2.83	$\Delta (8 \rightarrow 9)$
	3.03; 3.07		2.94; 2.95	$L_3 \rightarrow L_1; A_3 \rightarrow A_1^+$
	3.2		3.17	$L_2 \rightarrow L_1$
3.35	3.23	3.22	3.3	(8 $\rightarrow$ 9) Volume effect.
		3.3	3.5	$M_1 \rightarrow M_1^+$
		3.5	3.8	(8 $\rightarrow$ 9; 7 $\rightarrow$ 9) volume effect
5.0		4.8	4.9	(7 $\rightarrow$ 10) volume effect.
(a) Ref. 1				
(b) Ref. 5				
(c) piezotransmission (80 K).				

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9. RESONANT RAMAN SCATTERING IN HfS₂

Tai C. Chiang and Y. Ron Shen

In recent years, there has been an increasing interest in the experimental and theoretical studies of layered compounds. HfS₂ is a layered semiconductor with good quality samples readily obtainable. There are four phonon modes: A_{2u} and E_u which are IR active; A_{1g} and E_g which are Raman active. The E_u mode has been studied extensively by IR reflectance measurements and A_{1g} and E_g modes have been observed by nonresonant Raman spectroscopy. Band structure calculation has been carried out by several groups using different schemes yielding very different results. Our work includes transmission, luminescence and resonant Raman spectroscopy at different temperatures. Our transmission measurement results agree very well with those in the literatures and show no sharp structure at liquid nitrogen temperature near the absorption edge in the region between 1.9 eV and 2.65 eV although the absorption coefficient increases from essentially zero to $\sim 1.4 \times 10^4 \text{ cm}^{-1}$. The long tail

of the absorption coefficient implies this is an indirect-gap semiconductor with a gap energy around 2 eV at $\sim 80^\circ\text{K}$. We have not been able to detect luminescence from our sample even at 1.6°K under different excitation frequencies. It is not known whether this is an intrinsic property of the crystal. Polarized Raman scattering results show unambiguously the two modes E_g and A_{1g} at 263 cm⁻¹ and 337 cm⁻¹, respectively. We have also studied the dispersion of the resonant Raman cross sections by using tunable CW dye lasers and discrete lines from the Ar⁺ laser. The two modes show essentially the same resonant enhancement which appears to be much smaller compared to the corresponding increase in the absorption coefficient. This fact also suggests that the absorption edge is due to indirect transitions. There has been no evidence of two-phonon resonant enhancement near the indirect gap. The onset of two-phonon modes is around 2.3 eV which we believe is a good indication of the position of the direct gap.

10. RESEARCH PLANS FOR CALENDAR YEAR 1977

Y. Ron Shen

We plan to continue our collaboration with Prof. Y. T. Lee's group on molecular beam studies of multiphoton dissociation of polyatomic molecules. We will investigate the dissociation dynamics, the excitation mechanism, the collisional effects, isotope selectivity, etc. Using tunable dye lasers, we shall continue our studies on nonlinear optical mixing in metal vapor. We will look into the possibility of using the resonant forbidden processes to generate tunable coherent

radiation in the infrared as well as measuring the forbidden transition matrix elements. We shall use the four-wave mixing technique to study excitons, phonons, and magnons in solids. We are also developing a new nonlinear optical spectroscopic technique which will enable us to easily measure all the low-frequency excitations in a medium. We shall continue our work on surface polaritons. We will try to detect surface plasmons, and to study the effect of surface contamination on surface plasmon characteristics. Other programs involving resonant Raman scattering, resonant Brillouin scattering, luminescence, and resonant fluorescence in solids will also be continued. Linear and nonlinear optical effects in liquid crystals will be carried out with partial support from NSF.

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c. Research on Superconductors and Superconducting Devices

John Clarke, Principal Investigator

1. GEOPHYSICAL MEASUREMENTS WITH SQUIDS*

T. D. Gamble, W. M. Goubau, and J. Clarke

Ionospheric and magnetospheric disturbances generate electromagnetic radiation that is incident on the earth. By simultaneously measuring orthogonal components of the magnetic and electric fields at the surface of the earth one can determine the electrical resistivity deep below the surface. The probing depth is approximately the skin depth, which may be as large as 50 km for radiation at 10^{-3} Hz. These magnetotelluric (MT) measurements are of high current interest in at least two areas of geophysics. First, by surveying for regions of anomalously low resistivity one can locate high subsurface water content. The correlation of this data with other geological data (for example, heat flow) may provide a means of locating geothermal sources. Second, there is growing evidence that the resistivity of the ground changes with time as stress fractures in the rocks develop prior to an earthquake. Thus, continuous MT measurements at fixed sites on a fault may enable one to predict the onset of earthquake activity.

The development of magnetometers based on Superconducting Quantum Interference Devices (SQUIDS) offers a considerable increase in the sensitivity of the magnetic field measurements compared with the induction coils or flux-gate magnetometers used in the past. Our dc SQUID magnetometer (see MMRD Annual Report of last year, LBL-4550) has a sensitivity of 10^{-10} G Hz^{-1/2}, a dynamic range of $\pm 3 \times 10^6$ in a 1 Hz bandwidth, a slewing rate of 0.5 G s^{-1} , and a frequency response that is flat from 0 to 30 kHz. The high slewing rate and frequency response are essential to prevent transient overloads from spherics.

In collaboration with Professor H. F. Morrison and his students, we have completed two MT surveys at Leach Hot Springs in Grass Valley, Nevada. This hot spring is a known source of geothermal energy. In Fig. 1 we plot orthogonal components of the apparent resistivity vs. the square root of the measurement period for a station directly above the hot springs. These data were obtained in the first survey during September 1975. A large decrease in resistivity is observed between 1 and 3 s^{1/2}. This anomaly is two orders of magnitude greater than any structure observed at sites 1.5 km to either side of the hot springs (see Fig. 2). No other geophysical measurements have revealed an anomaly of this magnitude. During July 1976 we resurveyed the area, and obtained data that confirmed the magnitude and location of the anomaly, thereby demonstrating the reproducibility of the technique.

The accuracy of the data near the resistivity minimum is relatively poor because of the reduction in the electric field signals resulting from the lower apparent resistivity. Therefore, the magnitude of the dip, while reproducible, is somewhat uncertain. The onset of the dip as a function

of measurement period is sharper than can be accounted for entirely by variations with depth of the electrical conductivity of the ground. Seismic studies show that three fault lines intersect at the hot springs. We feel that the dip is probably caused by an anisotropy arising from highly conductive hot water saturating the fault lines.

So far, we have used conventional methods to process our MT data. We thus obtain a 2x2

Fig. 1. Rotated apparent resistivity vs. square root of period at a site directly above Leach Hot Springs.
(XBL 7612-7924)

Fig. 2. Rotated apparent resistivity vs. square root of period at a site 1.5 km away from Leach Hot Springs. (XBL 7612-7923)

impedance tensor, which is rotated (for each frequency component) to find the "strike" direction. Finally, the apparent resistivities ρ_x (x parallel to strike) and ρ_y (y perpendicular to strike) are calculated (see Figs. 1 and 2). A shortcoming of this technique is that no noise analysis is possible, and that the impedances can be systematically biased to either higher or lower values depending on whether the noise is in the electric or magnetic field. We are currently investigating an analysis technique that may enable us to obtain unbiased apparent resistivities. This technique, if successful, would greatly improve the reliability of MT data.

In our opinion, SQUID technology has become sufficiently reliable that MT measurements using SQUID magnetometers can be made on a routine basis. The technique appears to have considerable potential as a survey tool. Our future plans are directed more towards a study of possible changes in resistivity that may precede an earthquake. We hope to establish at least two MT stations on the San Andreas Fault, near Hollister, in order to monitor the apparent resistivity of the fault over a period of at least one year.

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2. INTEGRATED THIN-FILM SUPERCONDUCTING GRADIOMETER*

J. Clarke, W. M. Goubau, and M. B. Ketchen

Superconducting SQUID-based gradiometers that detect extremely small changes in magnetic field gradients are of importance in certain areas of medical and geophysical research. The advantage of a gradiometer over a magnetometer is the ability to discriminate against fields generated by distant sources (such as magnetospheric magnetic noise) in favor of fields generated by nearby sources (such as the human heart). This rejection of background noise often results in a greatly improved signal-to-noise ratio, and allows investigation of tiny signals that would otherwise be lost in the background noise.

We have fabricated a prototype integrated thin-film gradiometer in which the SQUID and superconducting pick-up loops are deposited on a single $90 \times 20 \times 10$ mm substrate (see Fig. 1). If the rectangular pick-up loops are identical, a uniform magnetic field H_z applied at right angles to the plane of the loops induces zero supercurrent in the niobium cross-strip. A magnetic field applied in the x-y plane induces no currents provided that the structure is completely planar. On the other hand, a magnetic field for which $\partial H_z / \partial x$ is nonzero does induce a supercurrent in the niobium strip. This current is proportional to $\partial H_z / \partial x$. The supercurrent is detected by a tunnel junction dc SQUID that is deposited on the niobium strip, as shown in Fig. 1.

In a practical device, the two loops are not identical, and the gradiometer must be balanced. Balance is achieved by adjusting the positions of two glass blocks (see Fig. 1) on each of which is deposited a niobium film. The blocks are mounted in a carriage and spring-loaded so that the films are pressed against the gradiometer substrate. The blocks can be moved, as indicated, in the plane of the gradiometer by means of a differential screw that is operated from outside the cryostat. A balance of better than 10 ppm is readily achievable. The insensitivity to fields in the x-y plane is of comparable magnitude.

Fig. 1. Plan view of dc SQUID thin film gradiometer. (XBL 767-7215A)

The measured rms noise of the SQUID above 5×10^{-2} Hz is about $8 \times 10^{-5} \phi_0 \text{ Hz}^{-1/2}$; below 5×10^{-2} Hz, the power spectrum exhibits a $1/f$ behavior (f is the frequency). Above 5×10^{-2} Hz, the

measured noise and the measured response of the gradiometer correspond to a gradiometer sensitivity of $2 \times 10^{-10} \text{ G cm}^{-1} \text{ Hz}^{-1/2}$.

We have recently constructed a larger version of the gradiometer that is about five times longer and two times wider than the earlier version. The measured sensitivity is an order of magnitude greater, as expected. The final version of the device will be fabricated on an optically polished quartz substrate, and should therefore have very high rejection of magnetic fields in the x-y plane. We also hope to gain a further order-of-magnitude improvement in sensitivity through improved SQUID design.

Our ultimate goal is to develop a high sensitivity gradiometer whose balance characteristics are stable under repeated thermal cycling. Such devices would be particularly suitable for use under adverse conditions (for example, in geophysical measurements) where readjustment of the device is impractical. We plan to make use of this gradiometer in our geophysical program.

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3. NOISE CALCULATIONS FOR THE dc SQUID

C. D. Tesche and J. Clarke

The dc SQUID is an extremely sensitive detector of magnetic field fluctuations. It has important applications in geophysics and medical physics, as well as in numerous laboratory measurements. Although the SQUID has been in use for over a decade, no detailed calculations of its behavior or noise limitations have previously been made. In order to optimize the energy resolution of the SQUID, we have developed a computer model that enables us to calculate the performance of the device over the appropriate range of experimental parameters.

The SQUID consists of two shunted Josephson tunnel junctions, each with a critical current I_0 , a capacitance C , and a shunt resistance R , mounted on a superconducting ring of inductance L . The temperature is T . In order to avoid hysteresis in the current-voltage characteristics, we impose the constraint $2\pi I_0 R^2 C \leq \phi_0$, where ϕ_0 is the flux quantum. The SQUID is biased with a constant current I . The resultant average voltage V is then a periodic function of the flux ϕ_a applied to the SQUID. Small changes in ϕ_a are detected as changes in the voltage V . The ultimate flux resolution is limited by the Johnson noise generated in the resistive shunts, which appears as a voltage noise across the SQUID. The flux noise power spectrum is $S_\phi = S_V / (\partial V / \partial \phi_a)_I$, where S_V is the power spectrum of the voltage noise, and $(\partial V / \partial \phi_a)_I$ is the transfer function of the SQUID.

We modeled the SQUID by a set of differential equations for the time-varying voltage as a function of ϕ_a and the SQUID parameters I_0 , L , R , and T . The equations were integrated numerically on the LBL 7600 computer. S_V and $\partial V / \partial \phi_a$ were then

calculated for numerous values of the SQUID parameters. The energy resolution per Hz, $S_\phi / 2L$, can be expressed as

$$S_\phi / 2L = (\Gamma / \beta R) \zeta_\phi(\beta, \Gamma) \phi_0^2 / \pi \text{ (JHz}^{-1}\text{)}, \quad (1)$$

where $\Gamma = 2\pi k_B T / I_0 \phi_0$, $\beta = 2LI_0 / \phi_0$, and $\zeta_\phi(\beta, \Gamma)$ is the calculated flux noise power spectrum in dimensionless units. From computed curves of ζ_ϕ vs. I for various values of ϕ_a , I_0 , L , and T , we can optimize the energy resolution of the SQUID, given the range of experimentally available SQUID parameters. Because of the complexity of the SQUID behavior, previous approximate expressions for the energy resolution did not permit proper optimization of the performance of the dc SQUID.

In general, we find that SQUID performance tends to improve as the parameters (L/R) and T decrease. The least value of L is usually determined by fabrication difficulties and the need to inductively couple flux efficiently to the SQUID; a reasonable value for a cylindrical geometry is 0.35 nH. The smallest tunnel junctions that we anticipate fabricating have a capacitance of about 1 pF. To obtain nonhysteretic current-voltage characteristics, we therefore require $R^2 I_0 \leq 200 \Omega^2 \mu\text{A}$. For I_0 on the order of a few μA , ζ_ϕ is proportional to T , as expected. For fixed values of the temperature T and inductance L , $S_\phi / 2L$ is a function only of the junction critical current, I_0 , and the bias current, I . Our computed curves of $S_\phi / 2L$ vs. I for fixed I_0 exhibit minima that are rather broad for $\beta \leq 1$ and become progressively sharper as β is increased above unity. It is therefore disadvantageous to operate SQUIDs with β much higher than unity because $S_\phi / 2L$ then varies strongly with bias current.

In Fig. 1 we plot $S_\phi / 2L$ (minimized with respect

Fig. 1. $S_\phi / 2L$ vs. $\beta = I_0 (2L / \phi_0)$ for dc SQUID. (XBL 7612-7921)

to 1) vs. $\beta = I_0(2L/\phi_0)$. $S_\phi/2L$ is nearly independent of β for $1 \lesssim \beta \lesssim 15$. From this curve, and the desirability of having $S_\phi/2L$ relatively insensitive to bias current, we conclude that the optimum operating condition is $\beta \approx 1$, corresponding to $I_0 \approx 3 \mu\text{A}$, and $R \approx 4 \Omega$. With these values, $S_\phi/2L \approx 1.6 \times 10^{-32} \text{ JHz}^{-1}$ for a wide range of bias current.

SQUIDS with a new configuration are now under construction, with a choice of parameters guided by the results of these calculations. We expect to achieve a substantial improvement in sensitivity.

4. LOW FREQUENCY NOISE IN TIN FIBERS AT THE SUPERCONDUCTING TRANSITION

J. Clarke and M. B. Ketchen

Most measurements at low frequencies are limited in accuracy by "flicker noise." The power spectrum of this noise varies as $1/f$, where f is the frequency. A detailed understanding of the physical origin of $1/f$ noise is of considerable importance in improving the low frequency performance of many devices. Previously, we investigated the low frequency noise in metal films deposited on glass substrates. We showed that the $1/f$ noise in metal films at room temperature and in tin and lead films at the superconducting transition arises from equilibrium temperature fluctuations. A theory was developed to account for the magnitude of the noise. In the usual Brownian motion treatment, the fluctuations are temporally and spatially uncorrelated, with $c(\vec{s}) = \langle T(\vec{r} + \vec{s}, t) T(\vec{r}, t) \rangle \propto \delta(\vec{s})$. In the case of the thin metal films on substrates, however, the fluctuations were shown to be spatially correlated with $c(\vec{s}) \propto 1/|\vec{s}|$.

To investigate whether this correlation was a property of the metal itself or of the metal-substrate combination, we have recently performed a series of measurements on Sn strips that were not in contact with a substrate. The strips typically had a length (L) of 30 mm, a width of 50 μm , and a thickness of 2 μm . Some samples were made with a 100 nm thick lead coating on one side of the tin strip except for an uncovered region in the middle of length (ℓ) typically 2 mm. A few samples were made with a mean free path shortened by the addition of about 3% of In to the Sn. Each end of the Sn strip was held by two separate superconducting clamps that enabled us to obtain four-terminal current-voltage characteristics. The film was freely suspended between the two pairs of clamps. The clamps were attached to a copper plate mounted vertically in a vacuum can immersed in superfluid liquid helium. The temperature of the copper plate was maintained near the mid-point of the transition of the Sn strip by a heater. In this arrangement, heat can flow into the Sn film only at the ends; the configuration is thus an excellent approximation to a one-dimensional thermal system, for which the theory is relatively straightforward.

A steady current (typically a few microamperes) was passed through the Sn strip, and the steady voltage and noise voltage developed were measured

with a dc SQUID voltmeter. The resolution of the noise measurements was limited by Johnson noise in the sample. The fluctuating output of the voltmeter was digitized, and analyzed by a PDP-11 computer to obtain the power spectrum of the voltage fluctuations across the sample. The power spectrum of an In-doped sample with $L = 30 \text{ mm}$ and $\ell = 2 \text{ mm}$ is shown in Fig. 1. The power spectrum is white below about 5 Hz. This knee frequency is in good agreement with the value predicted by the thermal fluctuation model, $f_1 = D/\pi\ell^2 \approx 4 \text{ Hz}$ (with D , the thermal diffusivity estimated to be $100 \text{ cm}^2 \text{ sec}^{-1}$). At frequencies above 5 Hz, the power spectrum falls off roughly as $1/f$. Some samples exhibited a second knee at a frequency $f_2 = D/\pi L^2$: the slope was shallower than -1 above the knee, and steeper than -1 above the knee. (For the sample whose power spectrum is shown in Fig. 1, we predict f_2 to be about 1 kHz, a frequency outside our range of measurement.) The power spectra obtained agree more closely with the model based on uncorrelated fluctuations, where the slopes should be 0 ($f < f_1$), 0.5 ($f_1 < f < f_2$), and 1.5 ($f > f_2$), than with the model based on correlated fluctuations, where the slopes should be 0 ($f < f_1$), 1.5 ($f_1 < f < f_2$), and 2 ($f > f_2$).

This agreement was confirmed by experiments in which either a delta function or step function in power was applied to the sample, and the resulting change in resistance measured as a function of time. The cosine transforms of the responses to the delta and step functions are the power spectra for the uncorrelated and correlated cases respectively. In Fig. 1 we plot these two transforms. The shape of the transform of the delta

Fig. 1. Power spectra obtained from an In-doped Sn film. (XBL 7612-7922)

function response is in excellent agreement with the shape of the measured power spectrum, whereas the transform of the step function response has a quite different shape.

The measurements represent a considerable advance in our understanding of low frequency noise in metal films. In a freely-suspended film, the fluctuations are spatially uncorrelated [$c(\vec{s}) \propto \delta(\vec{s})$], while for a film deposited on a substrate, the fluctuations are spatially correlated [$c(\vec{s}) \propto 1/|\vec{s}|$]. Therefore, it appears that the $1/f$ noise observed in metal films on substrates arises not from fluctuations in the film alone, but from fluctuations that involve both the film and the substrate. However, in both cases, the noise arises from equilibrium temperature fluctuations: the interaction between the film and the substrate changes the shape of the power spectrum, but not the value of the mean square fluctuation. We plan to investigate the nature of the interaction in detail.

5. SUPERCONDUCTING TRANSITION EDGE BOLOMETER

J. Clarke, P. L. Richards, and N.-H. Yeh

Until recently, semiconducting bolometers have been the most sensitive wideband detectors of submillimeter wave radiation. The urgent need for more sensitive detectors for laboratory and astrophysical applications has led us to investigate alternative types of bolometer. We have developed a composite superconducting bolometer that has an optimum electrical NEP of $1.7 \times 10^{-15} \text{ W Hz}^{-1/2}$, the highest sensitivity presently available. The absorptivity in the far infrared is approximately 50%.

The configuration of the bolometer is shown in Fig. 1. An Al film about 50 nm thick is evaporated near one edge of a $4 \times 4 \times 0.035 \text{ mm}$ sapphire substrate as a temperature sensor. A Bi strip near the opposite edge is a heater for electrical calibration. The rear surface of the substrate is covered with an 80 nm thick Bi film to absorb the far infrared radiation. Four small rectangles of In are evaporated on the upper corners of the substrate, and cold welded to two $15 \mu\text{m}$ diameter In-coated nylon threads. The coated threads

Fig. 1. Configuration of composite superconducting bolometer. (XBL 7612-7932)

provide thermal conductance to the substrate and electrical conduction to the Al and Bi strips. The mount is suspended in a vacuum can immersed in liquid helium at about 1.1 K. The copper mount is electrically heated until the Al strip is roughly at the midpoint of the superconducting transition. When radiation is absorbed by the bolometer, the temperature of the bolometer rises. The resulting increase in the resistance of the Al strip is measured with suitable electronics. A feedback circuit maintains the temperature of the bolometer close to the midpoint of the transition.

The measured electrical NEP of our best bolometer as a function of frequency is shown in Fig. 2. The optimum NEP is $1.7 \times 10^{-15} \text{ W Hz}^{-1/2}$ at 2 Hz. The large decrease in sensitivity at low frequencies arises from drifts in the temperature of the helium bath. The dashed line represents the NEP calculated from the thermal and Johnson noise limitations; at low frequencies, a $1/f^2$ law has been fitted to the data to account for the bath temperature drifts. At 2 Hz, the measured NEP is about 50% higher than the thermal noise limit.

By means of separate transmittance experiments, we estimate the absorptivity of the Bi film to be approximately 50% in the range 3 to 300 cm^{-1} . This absorptivity has been confirmed (but less accurately) in a preliminary direct optical calibration. Far infrared radiation was coupled to the bolometer by a light-pipe containing an appropriate bandpass filter to reduce unwanted room temperature radiation. The response of the bolometer when the source of the radiation was alternated between 77 K and 300 K was measured. We hope to complete a more accurate far infrared calibration very shortly.

Several other bolometers of comparable performance have been successfully tested. With

Fig. 2. Measured (•) and theoretical (---) NEPs for superconducting bolometer. (XBL 7612-7925)

the completion of the far infrared calibration, the device will be ready for use in laboratory and astrophysical measurements. The NEP is about a factor of five better than values reported in the literature for small area semiconductor bolometers, and an order of magnitude better than composite semiconductor bolometers of comparable area. For certain low-background submillimeter applications, the transition edge bolometer can reduce the observation time for a given source by as much as two orders of magnitude compared with semiconductor bolometers. Thus, one can now undertake measurements of very weak sources that were previously unobservable.

6. MICROWAVE ENHANCEMENT OF THE SUPERCONDUCTING ENERGY GAP

T. R. Kommers and J. Clarke

Eliashberg and co-workers have reported calculations indicating that, under suitable conditions, the energy gap, Δ , of a superconducting thin film could be enhanced by microwave irradiation. In the Eliashberg model, the predominant effect of photons with energies $\hbar\omega < 2\Delta$ is to excite quasiparticles from states near the bottom of the excitation spectrum to states of higher energy. Thus, additional pair states with wavevectors near the Fermi wavevector, k_F , are available for occupancy. Since these pair states near k_F contribute most strongly to the pairing interaction, this redistribution of pair state occupancy increases the condensation energy, and results in an increase in Δ . Furthermore, Eliashberg suggested that the transition temperature of an irradiated film would be higher than its equilibrium value. Gap enhancement has been indirectly demonstrated by others: at a given temperature the critical current of a narrow superconducting film or point contact junction was found to be enhanced by photon or phonon irradiation.

We have made the first direct measurements of microwave stimulated gap enhancement using Al-Al₂O₃-Al quasiparticle tunnel junctions. The junctions were fabricated in a crossed film geometry, and mounted near the shorted end of an X-band waveguide so that the junctions coupled well to the electric field. The junctions were immersed directly in a temperature stabilized helium bath. The differential resistance of the junctions was plotted as a function of bias voltage on an x-y recorder. We found that there were sharp minima in the differential resistance at voltages $\pm(\Delta_1 - \Delta_2)$ and $\pm(\Delta_1 + \Delta_2)$, where subscripts 1 and 2 refer to the two Al films forming the junction. As a check on our method of measuring Δ , we plotted Δ_1 and Δ_2 against temperature and found good agreement with the BCS theory.

The differential resistance was also measured in the presence of varying levels of microwave power. For modest power levels (< 20 mW delivered to the waveguide) sharp minima in the differential resistance were again observed at $\pm(\Delta_1 - \Delta_2)$ and $\pm(\Delta_1 + \Delta_2)$. Additional minima were also observed at bias voltages $\pm(\Delta_1 - \Delta_2) \pm n\hbar\omega$ and $\pm(\Delta_1 + \Delta_2) \pm n\hbar\omega$ ($n = 1, 2, \dots$) due to photon assisted tunneling.

In Fig. 1 we present results obtained for an Al junction evaporated on Ba F₂, a material that enables phonons to escape rapidly from the junction into the substrate. This junction had films with substantially different transition temperatures. The results given in Fig. 1 are for the film with the smaller gap (lower T_c). Curve (a) is 2Δ in the absence of microwaves, and curve (b) is 2Δ in the presence of constant applied microwave power, in this case, 1 mW at 9.9 GHz. A large increase in 2Δ is evident: at 1.195 K, the gap is almost doubled.

A detailed study of gap enhancement is now being made. We are particularly interested in the values of Δ at or above the equilibrium transition temperature, and in the nature of the phase transition between the superconducting and normal states in the presence of microwaves. We also plan to study the effect of different substrates on the enhancement. When the phonons are trapped in the junction because of poor coupling between film and substrate, we expect the enhancement to be qualitatively different than when there is good thermal coupling. From these experiments, we hope to obtain detailed information on the relaxation processes that occur in superconductors perturbed from equilibrium.

Fig. 1. 2Δ vs. temperature for one film of an Al-Al₂O₃-Al tunnel junction (a) without microwaves, and (b) in the presence of microwaves. (XBL 7612-7920)

7. RESEARCH PLANS FOR CALENDAR YEAR 1977

John Clarke

The magnetotelluric technique will be applied to other areas to search for geothermal sources. We hope to establish two (or more) magnetotelluric stations on the San Andreas Fault near Hollister to make long term measurements of the apparent resistivity along the fault. If changes in

resistivity can be measured, they may represent an earthquake precursor. These stations will also be used in three subsidiary experiments: the long term stability of our SQUID magnetometers will be investigated; changes in the ambient magnetic field will be measured, and compared with the data obtained from existing stations; and, by subtracting signals from the two magnetometers, we hope to obtain data on magnetic gradient fluctuations that originate from within the fault, and that could also represent earthquake precursors.

A thin film integrated gradiometer is to be fabricated on an optically polished quartz substrate; its performance will be carefully determined. We are interested in the sensitivity of the device, the degree of balance that can be achieved, and its long term stability. If the expected performance is obtained, we hope to operate the device in the field to look for magnetic gradient fluctuations in areas of high inhomogeneity, such as a fault. The gradiometer could also be used to take magnetocardiograms and magnetoencephalograms.

We will undertake further work on low frequency $1/f$ noise in metal films on insulating substrates. The experiments will be directed towards understanding processes at the metal-substrate interface, which is now believed to play an important role in the noise generation. This work may ultimately result in devices with reduced $1/f$ noise.

The program on nonequilibrium processes in superconductors will be expanded. The work described on the microwave-enhancement of the superconducting energy gap, Δ , will be continued. We will make measurements of Δ vs. temperature as a function of microwave power near the transition temperature to investigate the nature of the superconducting transition. The work will be extended to lower microwave frequencies, and to other metals. The effects of changing the nature of the substrate on which the films are deposited will be studied. A new experiment will be undertaken to measure the quasiparticle branch mixing time in aluminum. This experiment has two goals. First, we will determine the electron-phonon scattering time. Second, we will measure the branch mixing time as a function of quasiparticle energy to see if an enhancement in the branch mixing rate occurs at 3Δ due to direct electron-electron scattering. This enhancement has been predicted theoretically. These two sets of experiments are expected to produce a considerable amount of information on the nature of relaxation processes in superconductors. These processes are not only of fundamental interest, but are also likely to be important in the understanding of superconducting microbridges, and in the design of superconducting cavities.

An apparatus for measuring very small magnetic susceptibilities at low temperatures, using a dc SQUID as a detector, is to be constructed. An immediate application is to the measurement of the susceptibility of electron-hole drops in germanium, in collaboration with Professor Jeffries and his

group. The susceptometer will also be available for more routine measurements.

8. 1976 PUBLICATIONS AND REPORTS

John Clarke and Associates

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2. R. F. Voss and J. Clarke, Flicker ($1/f$) Noise: Equilibrium Temperature and Resistance Fluctuations, Phys. Rev. B 13, 556 (1976) (LBL-4109).
3. R. F. Voss and J. Clarke, $1/f$ Noise from Systems in Thermal Equilibrium, Phys. Rev. Lett. 36, 42 (1976) (LBL-3969).
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7. J. Clarke and T. Y. Hsiang, Low-Frequency Noise in Tin and Lead Films at the Superconducting Transition, Phys. Rev. B 13, 4790 (1976) (LBL-4535).
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1. C. D. Tesche and J. Clarke, A Computer Model for Noise in the dc SQUID, Proceedings of the 1976 Applied Superconductivity Conference, Stanford, California, LBL-5461.
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4. J. Clarke, Current Performance of Superconducting Quantum Interference Devices, Proceedings of the Conference on Superconducting Quantum

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N.-H. Yeh, Superconducting Bolometers for
Submillimeter Wavelengths, to be submitted to
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6. M. L. Rappaport, The Resistance of Super-
conducting-Normal Metal-Superconducting Sandwiches
(Ph.D. Thesis), LBL-5473, September 1976.

Lectures and Seminars 1976-77

1. "1/f Noise in Metals, Josephson Junctions, and
Music," seminar at the Department of Physics,
U.C.L.A., January 21, 1976.
2. "Music is Noise: Noise is Music," talk at the
University Art Museum in the Wednesday Noon
Lecture Series, February 18, 1976.
3. "Application of Superconductivity," talk to
Berkeley Physics Undergraduate Association,
March 3, 1976.
4. "1/f Noise," seminar in the Department of
Electrical Engineering, U.C. Berkeley, March 15,
1976.
5. "Quasiparticle Branch Imbalance in Super-
conductors," invited paper at the March meeting
of the A.P.S., Atlanta, Georgia, March 29, 1976.
6. "1/f Noise in Metals, Superconductors, and
Josephson Junctions," seminar at National Bureau
of Standards, Washington, D.C., April 2, 1976.
7. "1/f Noise in Metals, Superconductors, and
Josephson Junctions," seminar at Bell Telephone
Laboratories, Murray Hill, N.J., April 6, 1976.
8. "Applications of the Josephson Effects,"
colloquium at the Department of Physics, University
of Brasilia, Brasilia, Brazil, May 7, 1976.
9. "SQUIDS - and Their Applications," seminar at
the Department of Physics, Pontifica Universidade
Catolica, Rio de Janeiro, Brazil, May 14, 1976.
10. "1/f Noise in Metals and Music," seminar for
Alvarez Group, U.C. Berkeley, June 21, 1976.
11. "1/f Noise - An Equilibrium Phenomenon,"
invited talk at Gordon Conference, Tilton, N.H.,
July 21, 1976.
12. "Low Frequency Noise in SQUIDS," invited
lecture at Summer Study on Superconductive
Electronics, U.S. Naval Postgraduate School,
Monterey, California, August 3, 1976.
- *13. "Thin-Film dc SQUID Gradiometer," M. B.
Ketchen, W. M. Goubau, J. Clarke, and G. B.
Donaldson, poster session at 1976 Applied Super-
conductivity Conference, Stanford University,
August 17-20, 1976.
14. "A Computer Model for Noise in the dc SQUID,"
C. D. Tesche and J. Clarke, talk given (by
C. D. Tesche) at the 1976 Applied Superconductivity
Conference, Stanford University, August 17-20,
1976.
15. "Superconducting Quantum Interference Devices,"
series of four lectures given at the NATO
Advanced Study Institute on Small Scale Super-
conducting Devices, Gardone Riviera, Italy,
Sept. 1-10, 1976.
16. "Microwave Enhancement of the Superconducting
Energy Gap," seminar at the Department of Physics,
H. C. Orsted Institute, Copenhagen, Denmark,
September 21, 1976.
17. "Applications of Superconducting Quantum
Interference Devices," invited talk at the Annual
Meeting of the Austrian Physical Society, Linz,
Austria, September 29, 1976.
18. "Low Frequency Applications of Low Frequency
Superconducting Interference Devices," invited
talk at IC-SQUID, International Conference on
Superconducting Quantum Devices, Berlin, Germany,
October 6, 1976.
- *19. "Integrated Thin Film dc SQUID Gradiometer,"
talk given by G. B. Donaldson at IC-SQUID,
International Conference on Superconducting
Quantum Devices, Berlin, Germany, October 8, 1976.
20. "Summary and Conclusions," invited summary
at IC-SQUID, International Conference on Super-
conducting Quantum Devices, Berlin, Germany,
October 8, 1976.

d. Excited Quantum Fluids in Solids

Carson D. Jeffries, Principal Investigator

Introduction. Several years ago it was established by Soviet physicists that electrons and holes in semiconductors subject to intense optical excitation could condense into an electron-hole liquid. This is a novel state of matter: the liquid has both quantum and classical properties; it undergoes a gas-liquid phase transition much like the water vapor-fog-droplet transition. These small electron hole droplets (EHD) can move freely within the crystal up to the velocity of sound. The liquid medium can also be viewed as an anisotropic multicomponent plasma of constant density; it is the first example of a Fermi liquid in a periodic lattice, and as such is of high theoretical interest. Our work has concentrated on a detailed, quantitative study of this liquid in germanium: we have developed methods for confinement of sizeable (1 mm^3) volumes of the liquid in potential wells of crystal strain; unravelled droplet nucleation and buildup phenomena; observed Alfvén wave plasma resonance in large single drops; and measured several magneto-oscillatory phenomena characteristic of Fermi liquids. It is becoming clear that these excited quantum fluids exist in several other materials and represent a general and important class of excitations of crystalline solids. We are receiving advice and collaboration from Professor C. Kittel on the theoretical aspects of these problems.

1. NUCLEATION PHENOMENA IN ELECTRON-HOLE DROPLET FORMATION*

Robert M. Westervelt, Eugene E. Haller, and Carson D. Jeffries

When a crystal of pure Ge at He^4 temperatures absorbs a photon an electron is excited up into the conduction band edge at the L point, Fig. 1, leaving a hole at the Γ point. This electron-hole (e-h) pair can be quickly (10^{-9} sec) bound by the Coulomb interaction into a free exciton (FE), with a binding energy of $E_x = 4 \text{ meV}$; its lifetime is $\sim 5 \text{ } \mu\text{sec}$; the FE are detected by phonon-assisted luminescence at 714 meV. Above a threshold density of FE, one observes a new luminescence line at 709 meV, revealing that the exciton gas has condensed into an electron-hole liquid (EHL) phase. We have succeeded in observing and explaining theoretically the full details of this transition, i.e., the nucleation process from FE to the EHD droplets. A schematic diagram Fig. 2, of the interior of a Ge crystal shows the formation of electrons and holes; excitons; possibly biexcitons or even higher exciton complexes (not yet experimentally observed); and a droplet embryo which, if larger than a critical size, grows into a macroscopic liquid EHD, of size $5 \text{ } \mu\text{m}$, with a constant density of $2 \times 10^{17} \text{ pairs/cm}^3$. The drop is maintained by condensation of FE on its surface (condensation energy $\phi = 2 \text{ meV}$ per pair), and decays by e-h recombination with a lifetime of $40 \text{ } \mu\text{sec}$.

Fig. 1. Band structure $E(k)$ for Ge, showing the indirect free exciton level E_x , and the liquid electron-hole drop band at E_B , with total Fermi energy E_F . (XBL 771-7368)

Fig. 2. Model of processes inside a Ge crystal leading to formation of electron-hole drops.

(XBL 771-7369)

Fig. 3. Luminescence of free excitons (FE) and electron-hole drops (EHD) in Ge as a function of optical excitation power P , monotonically increasing ("up"); and monotonically decreasing ("down") from a high level. This unique optical hysteresis is a consequence of droplet surface energy and finite lifetime.

(XBL 771-7370)

Fig. 4. EHD-FE phase diagram for pure Ge, including hysteresis effects; the liquid phase lies above, and the gas phase below these lines. The dotted line shows the theoretical coexistence curve for a hypothetical simple gas-liquid not displaying hysteresis.

(XBL 773-589)

We have discovered a remarkable "optical hysteresis" in the relative intensity of the FE luminescence and the EHD luminescence, giving for the first time direct evidence for the

existence of surface tension σ in the droplets. The relative intensities depend on the previous optical excitation history of the crystal, and point clearly to the existence of metastable states of the FE-EHD system. Figure 3 shows the FE and EHD luminescence as the optical pumping power P and hence the FE density is monotonically increased ("up" curve); an EHD threshold is observed at $P = 3 \text{ mW cm}^{-2}$. However, as P is monotonically decreased from a high level ("down" curve) the cut-off threshold occurs at $P = 1 \text{ mW cm}^{-2}$. Physically this means that the FE gas must be initially supersaturated to force an embryo to grow against the collapsing pressure arising from surface tension. Data of Fig. 3, together with Westervelt's detailed theory, yield $\sigma(o) = (2.6 \pm 0.3) \times 10^{-4} \text{ erg cm}^{-2}$, in good agreement with the most recent theoretical prediction for the surface tension. The pair density has been measured for up-going and down-going thresholds at various temperatures yielding the phase diagram, Fig. 4; there is excellent agreement with the theory. These data yield a value $\phi = (1.9 \pm 0.2) \text{ meV}$ for the condensation energy. Above 1.3 K we find the hysteresis of the EHD-FE system to persist for a very long time--many hours; the detailed time dependence of the metastable state is also in good accord with the theory.

This is the first system to be investigated with a gas-liquid phase transition displaying the features of Figs. 3 and 4. They arise from surface tension in combination with the finite lifetimes of both the gas and liquid phases; they are excited states. The central ideas of

Fig. 5. Effective free energy difference for EHD in Ge vs. droplet radius.

(XBL 771-7371)

Westervelt's theory can be seen from Fig. 5, a plot of the free energy difference ψ (including surface energy, chemical potential, and finite lifetime effects) between an e-h pair in a free exciton and in the liquid, vs. droplet radius, for various values of the free exciton supersaturation ratio S , determined experimentally by the optical pumping intensity. For Ge at 2 K, to surmount the potential barrier requires $S = S_+ = 8.65$; at this point a nucleation current J_+ "turns on" and embryos grow to macroscopic drops, i.e., the up-going threshold begins. The pumping can be reduced to an intermediate value, say $S = 2.20$, where the drops are maintained at a stable radius R_S (Fig. 5). At excitation $S_- = 2.12$, the down-going threshold occurs.

To summarize, our careful experiments, done with special high-sensitivity IR detectors developed in collaboration with E.E. Haller, have revealed intrinsic and novel EHD nucleation phenomena in Ge, and a theory has been developed by Westervelt that explains the observations very well and yields measured values of several important parameters of the system. As to possible applications, we note that: (1) the optical hysteresis could be utilized in an optical memory device, and (2) volume supersaturation of a large Ge crystal just below the up-going threshold will create a three-dimensional space into which ionizing particles will provide nucleation centers for EHD condensation. The tracks could be made visible by imaging of the localized recombination radiation--somewhat like a self-luminous cloud chamber.

* This work is described at the end of this section in Refs. 2, 4, 5, 7, and 9 of Journals and Conference Proceedings, and in Ref. 2, of Reports.

2. FORMATION KINETICS OF ELECTRON-HOLE DROPLETS*

Jean L. Staehli, Robert M. Westervelt, Eugene E. Haller, and Carson D. Jeffries

Whereas the above study is concerned chiefly with steady-state phenomena, this experiment and theory are concerned with the quantitative details of the time evolution of a FE-EHD system following pulsed excitation--the objective being to measure concurrently both the FE and the EHD luminescence and to develop a theoretical model sufficiently accurate to deal with the actual experimental observations. Previous theoretical work (the Pokrovskii rate equations) did not take into account the primary event, namely, droplet nucleation, nor the effects of surface tension. New equations are introduced to do this, and are solved numerically to find the FE concentration n_x , the EHD size, and the EHD concentration N following a smooth step function of light excitation. These calculations show that the drop size and concentration are strongly affected by how fast the FE density reaches threshold; it is also predicted that this density will overshoot and then become clamped once nucleation begins. These predictions are fairly well verified by our

Fig. 1. Left: measured free exciton (FE) and electron-hole drop (EHD) luminescence in pure Ge following pulsed light excitation. Right: the predicted FE concentration n_x ; drop concentration N ; and e-h pair density n_d in the liquid phase--which should be compared to the measured EHD luminescence. (XBL 771-7372)

experiments. The pulse is a smooth step function of light at $1.52 \mu\text{m}$ near the band gap, which gets absorbed into the volume of the crystal rather than at the surface. Figure 1, left, shows the experimental results, and the right, the predicted behavior. In particular, the results show: (1) a delay in the onset of EHD luminescence after the FE gas has reached its peak due to the time it takes for droplet embryos (≈ 25 e-h pairs) to form; (2) then a slow build-up of the EHD luminescence as the embryos grow to macroscopic droplets; (3) an overshoot and clamping of the FE density, most clearly at 2.30 K, following nucleation. Although the agreement is not perfect, both the present experiment and theory are considerably more sophisticated than any previous work, and we conclude that we understand the kinetics fairly well.

* This work is described at the end of this section in Ref. 6 of Journals and Conference Proceedings and Ref. 5 of Reports.

3. CONFINEMENT OF LARGE ELECTRON-HOLE DROPS BY STRAIN POTENTIAL WELLS IN Ge*

Robert S. Markiewicz, James P. Wolfe, and Carson D. Jeffries

The preceding two articles dealt with the small EHD ($\sim 5 \mu\text{m}$) formed in pure unstressed Ge, denoted as the Ge(4:2) configuration; there are 4 degenerate electron bands and 2 degenerate hole bands. When the crystal is stressed this degeneracy is partially or wholly removed, leading to a reduced drop binding energy, reduced liquid density and a lowering of the band gap edge. We have developed a method of producing sizeable drops ($\sim 1 \text{ mm}$) of the EHL in suitable strain potential wells; this liquid corresponds to Ge(1:2), and we have measured a number of its properties. Using the known deformation potentials of Ge we have calculated numerically the stress tensor, the band edge shift ΔE_g , and the liquid energy shift ΔE_{EHL} , and the liquid energy shift ΔE_{EHL} vs. position in an inhomogeneously stressed crystal. Figure 1(a), insert, shows the experimental arrangement: a rounded nylon rod is pressed against a Ge crystal; the nylon deforms, making a contact of width $2a$. The solution to this classical Hertz contact problem is surprising; the maximum shear stress is located not at the contact but at a point inside the crystal. We have shown that the maximum drop energy lowering ΔE_{EHL} occurs at a point of maximum octahedral shear stress. The calculated energy shifts are plotted in Fig. 1(a) and (b); it is clear that there exists an approximately parabolic potential well about a point within the crystal, a distance $\sim a$ below the contact surface. When the crystal is excited by a laser beam anywhere near this well, then

the free carriers, excitons and small droplets are all accelerated by the strain gradient to the point of maximum shear stress. There they coalesce into a single mass of the liquid, in a "large drop".

Direct proof of this is shown in Fig. 2, a vidicon image of the recombination luminescence at $1.75 \mu\text{m}$ emitted by the EHL in a stressed Ge disk. Due to the anisotropy of the band gap shift with stress, we find both experimentally and theoretically that it is possible to form one, two, or four such large drops by applying stress along the $\langle 111 \rangle$, $\langle 110 \rangle$, and $\langle 100 \rangle$ crystal axes, respectively. For example, Fig. 3 shows the calculated band gap shift ΔE_g in a square crystal for stress along $\langle 110 \rangle$, and also along $\langle 100 \rangle$. The stress contours clearly show the potential wells. In the first case, in three dimensions there are actually two drops, one exactly behind the other; in the second case there are four wells. This is beautifully confirmed by the experiments, Fig. 4, which show vidicon images of the recombination luminescence from the drops in various stress geometries; in the top photos the luminescence is collected from the square face; in the lower photos, from a bottom edge, using a mirror. In addition we have calculated and observed birefringence patterns in these same crystals confirming the calculated

Fig. 1. (a) insert: nylon plunger pressing Ge crystal, producing potential well of shear strain within the crystal at $z = 0.5 \text{ mm}$; the curves show the calculated band gap shift ΔE_g and drop energy shift ΔE_{EHL} for $F = 10 \text{ kg}$ and $2a = 1.4 \text{ mm}$. (b) potential wells at $z = 0.5 \text{ mm}$ as a function of y . (XBL 771-7373)

Fig. 2. Photograph from an IR scanning vidicon of a large strain-confined electron-hole drop at $T = 2 \text{ K}$ in a 4 mm disk of Ge, stressed with a nylon screw, and pumped with a 25 mW Ar ion laser beam. Carriers, excitons, and small droplets are accelerated into the well, coalescing into a single drop of diameter $\approx 0.4 \text{ mm}$. This image is formed directly from the recombination luminescence emitted by the liquid at $1.75 \mu\text{m}$. (XBB 771-630)

Fig. 3. Left: contours of constant band gap shift ΔE_g in Ge from a two-dimensional calculation for the stress geometry of Fig. 1(a). Right: contours for the geometry $F \parallel \langle 100 \rangle$.
(XBL 771-7393)

Fig. 4. Vidicon images of the recombination luminescence from large electron-hole drops confined in potential wells in Ge in various stress geometries. The upper photos are views from the square face, Fig. 1(a), insert; the lower photos are views through the supporting quartz plate.
(XBB 771-629)

strain distributions and the fact that the drops are located at points of maximum octahedral stress along $\langle 111 \rangle$ axes.

These are the first experiments to succeed in stably forming drops of sizeable volume, and they allow a number of new experiments, detailed below. In the context of plasma physics, this is an example of a cold, dense, compensated plasma (i.e., an electrical liquid) being stably confined by a potential well of strain energy, rather than by applied electromagnetic forces; the drops can be reproducibly maintained indefinitely in these wells.

Compared to the EHL in Ge(4:2), the liquid in stressed crystals, Ge(1:2), has a number of new properties: (1) the e-h pair density is lowered from $2.2 \times 10^{17} \text{ cm}^{-3}$ to $0.6 \times 10^{17} \text{ cm}^{-3}$; (2) the lifetime is increased from 40 μsec to 500 μsec ; (3) the binding energy is lowered from 5.9 meV to 4.5 meV; (4) the available drop radius is increased from 5 μm . These properties, as well as the number of drops and their location in the crystal can be understood theoretically.

*This work is described at the end of this section in Ref. 7 in Journals and Conference Proceedings and in Refs. 1 and 7 in Reports.

4. PROPERTIES OF THE ELECTRON-HOLE LIQUID IN Ge FROM LUMINESCENCE STUDIES*

Susan M. Kelso, John E. Furneaux, Robert S. Markiewicz, James P. Wolfe, and Carson D. Jeffries

A magnified luminescent image of a stressed crystal and its contents is sharply focused onto the entrance slit plane of a spectrometer via a precision x, y scanning mirror. We record the intensity I and the wavelength of the EHL recombination luminescence as a function of point of origin in the crystal in steady-state excitation and, additionally, as a function of time in the transient decay following fast laser turn-off. Figure 1 shows such time-resolved luminescence profiles at various times t following laser cut-off, showing the decay of the drop radius. By using mirrors we obtain luminescence profiles about three mutually perpendicular axes in the crystal, giving three-dimensional spatial information. This is done as a function of the applied force F from zero to 20 kg and at temperatures in the range $T = 1.6$ to 4.2 K.

At zero stress we observe a diffuse doorknob-shaped distribution of I_{EHL} (size $\sim 1 \text{ mm}$) centered on the axis of laser excitation; this is known to be a cloud of small droplets. We observe the usual excitation threshold for foramtion of EHD from FE, and a sharp decrease of I_{EHL} with increasing T . In transient decay the total I_{EHL} from the entire crystal has a decay time $\tau_d = 40 \mu\text{s}$ at 1.6 K, which becomes shorter at higher temperatures due to exciton boil off. The spatial distribution, however, does not change very much in this time.

As the applied stress is increased past a

Fig. 1. Time-resolved luminescence profiles from a large strain confined electron-hole drop in Ge. (XBL 771-7394)

threshold value $\approx 3 \text{ kg/mm}^2$, striking changes occur: the total intensity I_{EHL} increases by an order of magnitude; the decay time increases to $\tau_d \approx 500 \mu\text{s}$; the spectral line width of the EHL decreases from $\Delta E_0 = 3.4 \text{ meV}$ (at zero stress) to $\Delta E_\gamma = 2.4 \text{ meV}$; the luminescence is now seen to originate from a bright compact region fixed in the crystal at the point of maximum shear strain, and independent of the point of laser excitation. At low laser power ($P < 1 \text{ mW}$), τ_d and ΔE_γ are independent of P , indicating that the pair density in the EHL is essentially uniform over the potential well. Spatial scans of the distribution are consistent with hard-edged ellipsoids of EHL, approximately spherical. The steady-state radii increase as $P^{1/3}$ and display transient decay $r(t) \propto \exp(-t/3\tau_d)$. The decay time and total I_{EHL} are essentially independent of T , indicating that the strain gradient at the edges of the potential well greatly inhibits exciton boil off. The FE luminescence has not yet been observed at 1.6 K even at the lowest level of excitation. However, at 4.2 K as P is increased from zero, first the FE luminescence is observed, localized in the potential well; then there is a clear threshold for appearance of the EHL luminescence in the well. We believe that we observe a $\text{FE} \rightarrow \text{EHL}$ phase transition in Ge(1:2) in the potential well, analogous to that in unstressed Ge(4:2).

At 1.6 K and high excitation ($P > 100 \text{ mW}$) the well becomes filled and the large drop becomes distinctly nonspherical and takes the shape of the potential well (surface tension forces are orders of magnitude smaller than the bulk strain forces). The initial decay time is shortened to $\tau_d \approx 200 \mu\text{s}$, the luminescence linewidth becomes broadened and the drop volume begins to saturate with laser power; our preliminary interpretation is that we are observing compression of the liquid.

*This work is described at the end of this section in Ref. 7 in Journals and Conference Proceedings and in Refs. 1 and 7 in Reports.

5. ALFVÉN WAVE RESONANCE IN LARGE ELECTRON-HOLE DROPS

John E. Furneaux, Robert S. Markiewicz, James P. Wolfe, and Carson D. Jeffries

The EHL is a compensated plasma and can propagate Alfvén waves at microwave frequencies in magnetic fields greater than that for cyclotron resonances of the carriers. A magnetoplasma dimensional resonance, or standing Alfvén wave resonance, occurs when the Alfvén wavelength $\lambda_A = 2\pi H[4\pi n(m_e + m_h)]^{-1/2}$ becomes comparable to the diameter d of a strain-confined drop of the liquid, which can be measured simultaneously by luminescence imaging. From the measured field for resonance $H \propto \sqrt{n}$ we conclude that the density in the strain confined liquid is $n \approx 10^{17}$ pairs/cm³. The Alfvén resonance requires circulating currents throughout the entire drop and is neither theoretically expected nor observed for a cloud of small droplets. Alfvén resonance has also been used to study the fast build up kinetics of a large drop. Figure 1 shows the time-resolved microwave absorption at 25 GHz vs. magnetic field for a stressed Ge crystal at various times following cut-off of a 100 ns, 7 W laser pulse, which produces $\sim 10^{12}$ e-h pairs at the surface. The lines labeled E and H are the cyclotron resonances of free electrons and

Fig. 1. Alfvén wave resonances for a strain confined electron-hole drop in Ge observed at specified times following pulsed laser excitation. The drop diameter d is proportional to the resonant magnetic field, and these data yield $d(t)$.
(XBL 771-7391)

holes. After ~ 1.3 μ sec a new line is observed, moving toward higher fields. This is the Alfvén resonance $H \propto d$, of a growing drop, which builds up rapidly to a diameter $d = 300$ μ m and then decays in a time ~ 1500 μ sec. The initial delay is interpreted as the time it takes the e-h pairs to move 1 mm from the surface to the well minimum corresponding to an average velocity $\approx 10^5$ cm sec⁻¹.

*This work is described at the end of this section in Ref. 11 in Journals and Conference Proceedings and in Ref. 1 in Reports.

6. MAGNETO-ACOUSTIC ABSORPTION OF THE ELECTRON-HOLE LIQUID IN Ge*

Chuji Ohyama, A. D. A. Hansen, Jerry L. Turney, and Carson D. Jeffries

The availability of a large volume of electron-hole liquid in a strain well, pinned to a point fixed in the crystal, has made possible for the first time the direct observation of a structured magneto-acoustic absorption of ultrasonic waves, similar to that observed in other Fermi systems, e.g., Bi. When the EHL is subject to an applied magnetic field, the electron Landau levels will periodically cross the Fermi level as the field is increased. The consequent change in the density of states is seen as an increase in the acoustic absorption coefficient α with a periodicity proportional to H^{-1} , which provides a direct measurement of the Fermi level E_F of the liquid. Figure 1 shows the experimental arrangement used: two quartz ultrasonic transducers were bonded onto a pure Ge crystal subject to a variable stress, in which was formed a large drop by laser pumping between the transducers. An external field $H \leq 25$ kG could be applied either parallel or perpendicular to the propagation

Fig. 1. Experimental arrangement for observing magneto-oscillatory acoustic attenuation in the electron-hole liquid in Ge.

(XBL 773-587)

Fig. 2. Observed acoustic attenuation (c) for a single large drop in stressed Ge. The oscillations are proportional to H^{-1} and are due to the periodic crossing of the electron Landau levels with the Fermi level of the electrons in the liquid.

(XBL 773-588)

vector Q of the ultrasound. The EHL recombination luminescence was recorded along with changes in the acoustic attenuation in the frequency range 30 to 250 MHz. Figure 2(a) shows that for zero stress, and only small droplets present, no field dependence of the acoustic attenuation was observed. However for a large stressed drop, curve (b) with $H \perp Q$, we do indeed find a monotonic field dependence $\alpha(H) \propto [1 + (\omega_c \tau)^2]^{-1}$ as expected theoretically, where ω_c is the cyclotron frequency and τ is the inter-carrier collision time; these data yield $\tau = 6 \times 10^{-11}$ sec. Curves (c) and (d), with $H \parallel Q$, show a large magneto-oscillatory attenuation with a period $\Delta(1/H) = (3.3 \pm 0.2) \times 10^{-5} \text{ Gauss}^{-1}$, which yields an electron Fermi energy $E_F^e = 2.6 \pm 0.1 \text{ MeV}$ at $T = 1.8 \text{ K}$. Assuming only one electron ellipsoid is occupied we find for the e-h density $n = 6.2 \times 10^{16} \text{ pairs cm}^{-3}$ in the stressed EHL; this value agrees closely with that predicted for Ge(1:2). This is the most direct and accurate measurement of the density. This oscillatory experiment furthermore confirms the Fermi character of the liquid--this means that the electrons and holes are free, and are not bound into excitons inside the drop.

* This work is described at the end of this section in Refs. 10 and 12 of Journals and Conference Proceedings.

7. RESEARCH PLANS FOR CALENDAR YEAR 1977

Carson D. Jeffries

Ultra-pure Ge is still the ideal prototype material for study of electron-hole liquids,

which possess a wide variety of novel properties yet to be elucidated; we will use Ge in a number of related experiments as follows. A magnetic field has a pronounced effect on the shape of a large drop, due probably to a kind of dynamic diamagnetism from a net radial inward e-h pair current arising from surface condensation and internal recombination. A complete magneto-hydrodynamic theory of drops in magnetic fields will be attempted, including the effects of compressibility, viscosity, recombination magnetization, surface tension, and strain energy. This will be coordinated with detailed measurements designed to test the model. We have recent evidence for compressibility effects, and will measure the compressibility of the liquid in a strain well. We plan to study by time-resolved slit scan imaging spectroscopy the details of the formation of the confined drop: What flows (carriers, excitons or small droplets?) into the well and how fast? We will attempt a complete experimental and theoretical investigation of the kinetics of drop confinement in potential wells. We have some evidence of plasma instabilities in the FE-EHD system, particularly in wells; this will be further explored. We will extend the scope to study the kinetics of explosive formation of clouds of small droplets in unstressed crystals.

We plan experiments at higher stress to attempt to reach the fully degenerate Ge(1:1) configuration, which should be characterized by a much lower density and longer lifetime. It has been reported that microwave eddy current heating will explode drops; we will do some more quantitative experiments. It is of interest to measure carefully the magnetic susceptibility of EHD; this will be done by using r-f bridge techniques and also in collaboration with Prof. John Clarke's group using an ultrasensitive superconducting method. Such exotic properties as superfluidity, superconductivity, and ferromagnetism cannot be excluded from the realm of possibility. A detailed theory of Alfvén wave resonance now in progress will be completed. It may be possible to bunch small droplets into sheets with standing ultrasound waves: this would create a variable two-dimensional plasma grating. No definitive measurement of the diffusion coefficient for droplets exists. We will attempt a sophisticated measurement of this important parameter. Likewise a measurement of the Richardson thermionic evaporation coefficient of pairs from the droplet surface will be attempted. A phase diagram for the EHL in Ge(4:2) has been measured; we will attempt to do this next for Ge(1:2). The possible transient existence of biexcitons and higher excitonic molecules in the formation of the drop (a Fermi system) from excitons (Bose particles) is ripe for investigation by careful and high-sensitivity spectroscopy; we are equipping to do this.

The wide variety of these proposed experiments is characteristic of our multidisciplinary approach to the electron-hole liquid, and are an attempt to measure concurrently and to explain by a common theoretical model a large number of properties of this novel state. Finally, the studies in Ge will be extended to other materials:

Si, stressed GaAs, and insulating crystals.

8. 1976 PUBLICATIONS AND REPORTS

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2. R. M. Westervelt, J. L. Staehli, E. E. Haller, and C. D. Jeffries, Nucleation Phenomena in Electron-hole Drop Formation in Ultra-pure Ge, Oji Conference on Physics of Highly Excited States in Solids, Tomakomai, Japan, published in *Lecture Notes in Physics*, vol. 57 (Springer-Verlag, Heidelberg, 1976), p. 271.
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2. R. M. Westervelt, Experimental and Theoretical Analysis of Electron-hole Drop Nucleation Phenomena in Ultra-pure Ge, paper presented at XIII International Conference on Physics of Semiconductors, Rome, Italy, Aug. 30-Sept. 3, 1976; to be published in conference proceedings.
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4. J. P. Wolfe, J. E. Furneaux, and R. S. Markiewicz, Magnetostriction of an Electron-hole Drop in Ge, paper presented at XIII International Conference on Physics of Semiconductors, Rome, Italy, Aug. 30-Sept. 3, 1976; to be published in conference proceedings.
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2. THEORETICAL RESEARCH

a. Theoretical Solid State Physics

Marvin L. Cohen, Principal Investigator

1. SURFACE STATES ON CLEAN SEMICONDUCTORS*

M. L. Cohen, J. R. Chelikowsky, M. Schlüter, and S. G. Louie

We have continued to use the self-consistent pseudopotential method for calculating the electronic structure of semiconductor surfaces. This method which was developed by our group over the last two years is described in a block diagram in Fig. 1. Self-consistency in the sense used in these calculations requires that the charge density at the surface of a semiconductor is allowed to redistribute to accommodate the perturbation caused by the surface itself. The steps described in Fig. 1 involve the following procedures. First a potential is chosen which is empirically adjusted to give the correct bulk band structure.

STEPS IN ACHIEVING SELF-CONSISTENCY

Fig. 1. Block diagram indicating the basic steps in obtaining a self-consistent potential.
(XBL 771-7374)

Schrödinger's equation is then solved and the resulting wave function is used to calculate the charge density. Using Poisson's equation the

charge density allows a calculation of a Hartree potential and an exchange potential. The exchange potential is calculated only approximately using Slater's statistical exchange model. More sophisticated models have also been used but the basic approach for the exchange potential is the X- α approach. The Hartree and exchange potential are then added to give a total screening potential. The structure and model parameters characteristic of the surface are then used to determine the geometrical constraints. This finally gives us a total potential which includes the potential coming from the ions and this potential is then used in the loop to solve Schrödinger's equation again. Because the charge density now has an opportunity to readjust to the surface perturbations, the system attempts to achieve self-consistency and after several trials, and using numerical methods to cut down on the number of trials, self-consistency is achieved.

The resulting calculations yield an excellent spectrum for the semiconductor surface. The charge densities of the surface states can be computed and the local density of states can also be evaluated. A number of crystals have been investigated and the results are among the best available using any method at this time. Silicon was used as a model of the group IV semiconductor materials. The local density of states was calculated as a function of layer distance into the semiconductor. The surface local density of states illustrates the characteristic dangling bond state which exists in the semiconductor gap. This is illustrated in Fig. 2 along with the total charge calculated for the coordinate z perpendicular to the surface. The x and y components have been averaged. The surface is relaxed by about one third of an Angstrom for this calculation. The use of the local density of states for illustrating and finding surface states is demonstrated by this application to silicon.

The III-V and II-VI zincblende materials have been investigated using GaAs and ZnSe as prototypes. Again the local density of states is used to find surface state characteristics. In particular the dangling bond surface states for both a Ga terminated surface and an As terminated surface have been investigated. The electronic charge density for these states is illustrated in Fig. 3. The characteristic features of these charge densities is their localization close to the terminating atom. The As dangling bond state is located in energy (for the most part) below the valence and maximum and does not extend into the optical gap. This result is in agreement with current experiment. The Ga dangling bond is located in energy just below the conduction band minimum if relaxation is not included. With relaxation this state merges with the conduction

Fig. 2. Local density of states (LDOS) for six atomic layers parallel to the Si (111) surface. The most prominent surface states are indicated. The total charge as a function of the coordinate perpendicular to the surface is shown for reference. (XBL 771-7375)

band. At present experimental results are unclear. Early results tended to give this state in the optical gap, but more recent results appear to be consistent with a gallium state in the conduction band. We have used relaxed models and have repositioned the Ga and As atoms near the surface in an attempt to obtain spectra consistent with experiment. At this point the problem is not solved. Almost all subsequent theoretical calculations done by other groups are in agreement with our results, but these do not agree with most recent experimental results. The question remains open and is an interesting one.

The properties of ZnSe were also investigated and the results are to a large extent similar to those of GaAs.

* Partially supported by NSF.

Fig. 3. Charge density of GaAs (110) surface for (a) Ga dangling-bond and (b) As dangling-bond surface states in the (110) plane terminated on the (a) Ga and (b) As atom. The charge density has been normalized to one electron per unit cell volume $\Omega_{\text{cell}} = 8.12 \text{ \AA}^3$. The contour spacing is in units of 2.0. (XBL 771-7376)

2. ELECTRONS AT STEPS, VACANCIES AND ADSORBATES ON SEMICONDUCTORS*

M. L. Cohen, S. G. Louie, M. Schlüter, J. R. Chelikowsky, K. M. Ho, J. E. Rowe and G. Margaritondo

We have applied the method described in preceding article No. 1 to local configurations such as steps, vacancies, and adsorbates on semiconductors. The importance of steps in catalysis and the importance of the electron structure of adsorbates is widely acclaimed in both the physics and chemistry literature. The models we have used are admittedly simple, but they do give some indication of the underlying physical effects.

The step surface was simulated by a ten-layer slab with surface atoms removed periodically to

form steps. An appropriate cell was chosen and the calculation was done in the self-consistent manner described in preceding article No. 1. It was found that the dangling bond surface states are strongly affected by the presence of steps. New states whose wavefunctions are localized along the step edges gave rise to additional structure in the density of states in the vicinity of the fundamental gap. Similar structure has been observed in recent photoemission experiments. The calculations indicate that step edges attract electrons from the surrounding step terraces. Regions of metallic behavior are expected in the absence of any reconstruction along the edges.

Although we have not applied the method used above to a surface vacancy, we expect results similar to our calculations for the bulk vacancy of silicon. In this case it was found that the ideal unreconstructed vacancy calculation gave states which exist in the silicon thermal gap. These states are predominantly dangling bond p-like localized on the four atoms surrounding the vacancy. The ideal unreconstructed vacancy yields an electronic spectrum which is unstable to Jahn-Teller type distortions. Various models for the reconstruction were examined to yield Jahn-Teller stable situations and the electronic structure of these models were investigated. The total charge density for a typical reconstruction model is given in Fig. 1. In this model the distances between the four atoms surrounding the vacancy are pair-wise increased resulting in a (100) uniaxial distortion and a net relaxation away from the vacancy. The essential result is that charge is removed from the vacancy region and is transferred into the back bonds.

Two problems connected with chemisorption on silicon (111) surfaces were examined. The first involved the investigation of hydrogen on silicon. Two structural models were explored: the mono-hydride and the tri-hydride configurations. The spectral results for the mono-hydride phase are in excellent agreement with earlier calculations and with experimental data obtained on hydrogenated surfaces starting with clean annealed (7x7) surfaces. The tri-hydride model was proposed by Pandey et al. to explain drastic spectral changes occurring for hydrogen adsorbed on a (1x1) quenched surface. Our calculations basically confirmed this conjecture but some discrepancies remain between the experimental and theoretical spectra. Possible explanations for the discrepancies have been proposed.

The second chemisorption problem which has been attacked with our self-consistent pseudopotential model is the configuration of chlorine on cleaved silicon (111) 2x1 surfaces. Using our detailed pseudopotential calculations and experimental measurements of the energy distribution and polarization selection rules for photoemission spectroscopy, we are able to rule out certain geometric configurations for the chlorine site. Specifically, strong p_z -symmetry polarization effects observed in photoemission and the results of our calculations allow us to rule out a possible three-fold coordinated ionic site for the chlorine atom on the silicon surface. The results of our work are consistent with a one-fold covalent site. The

Fig. 1. Total self-consistent valence charge density for a neutral Si vacancy in a reconstructed environment. Charge values are normalized to one electron per unit cell which extends over 53 atoms and one vacancy. (XBL 771-7377)

general use of this approach to determine chemisorption geometry is explored using this calculation as a prototype.

* Partially supported by NSF

3. METAL-SEMICONDUCTOR INTERFACES (SCHOTTKY BARRIERS)*

M. L. Cohen, S. G. Louie and J. R. Chelikowsky

We have applied the method described in preceding article No. 1 to an investigation of semiconductor metal interfaces. The calculation assumes a simplified model for the metal consisting of jellium having an electronic density equivalent to that of aluminum. The semiconductors considered were represented using self-consistent pseudopotentials. The interfaces which were studied in detail consisted of the (111) surface of silicon in contact with jellium, and then the

silicon was replaced by GaAs, ZnSe and ZnS using the (110) surface for these latter zincblende materials. The calculation was done in a fully self-consistent manner. The results yielded the characteristic features of the electronic structure for these interfaces.

There were several previous models used to explain the features of Schottky barriers. The Bardeen model involved the use of surface states to pin the Fermi level of the Schottky barrier. Heine later questioned the existence of surface states for an interface geometry. He proposed the existence of states which consisted of metal wavefunctions tailing deeply into the semiconductor region. Later Inkson suggested that conduction and valence band bending near the interface could explain Schottky barrier properties. Phillips also suggested a model in which the semiconductor and metal interacted in such a manner as to have chemical bonding between them.

The results of our numerical calculations prompted us to propose a theory of Schottky barrier properties which depended on metal induced gap states. These states were not identical in detail to the Heine states but did resemble them in many respects. The metal induced gap states consisted of metal wavefunctions with tails extending very short distances into the semiconductor. In fact, the tails tend to concentrate on the remnant of the surface state dangling bond regions which would exist if the semiconductor were interfaced with vacuum. These states pin the Fermi level and are responsible for the properties of the Schottky barriers.

The role of ionicity in Schottky barrier behavior has been discussed extensively in the literature. In particular if one replaces aluminum with other metals for group IV semiconductors like silicon, the barrier height is insensitive to this change. This is not true for semiconductors which are more ionic. The barrier height increases with electronegativity of the metal. The slope, S , of the barrier height vs. metal electronegativity is an important parameter for the behavior of Schottky barriers and it has been called the phenomenological index of interface behavior (studied by Kurtin, McGill and Mead). A plot of the index S as a function of semiconductor ionicity is given in Fig. 1. The behavior of this plot has been explored by a number of researchers. Using our model for the interfaces of aluminum (modeled by jellium) interfaced with Si, GaAs, ZnSe, and ZnS, we were able to calculate the parameter S and the barrier heights for these materials. The results were good agreement with experiment particularly for the less ionic materials.

The above results depended critically on the extent of the penetration of the tails of the metal induced gap states into the semiconductor. In Fig. 2 a plot of these tails is given for the semiconductors investigated. The silicon surface was (111) while the zincblende surfaces were (110) and this is responsible for the hump in the curve for silicon between $z=4$ and $z=5$. It is evident from the plot that the penetration for Si and GaAs is comparable, whereas the penetration is less for the more ionic Zn compounds.

Fig. 1. The index of interface behavior, S , vs. ΔX , the electronegativity difference of the anions and cations in the semiconductor. (After S. Kurtin, T. C. McGill, and C. A. Mead, Phys. Rev. Lett. 22, 1433 (1969). (XBL 771-7378)

Fig. 2. Charge distributions of the penetrating tails of the metal induced gap states in the semiconductor thermal gap. $\bar{p}(z)$ is the total charge density for these states averaged parallel to the interface with $z=0$ at the edge of the jellium core. (XBL 771-7379)

It is useful to use local density of states functions to explore the changes in the density of states in going from the metal side of the interface to the semiconductor side. In Fig. 3 the local density of states is plotted for six regions where the width of each region is approximately a Si-Si bond length. In Fig. 3

starting with the metal side of the Schottky barrier region I has the typical square root of energy behavior for a free electron metal. Region VI strongly resembles the bulk density of states of silicon. Region IV is the interface region, and it is evident that the gap which in bulk silicon would be void of states now contains a fairly large density of electronic states. These states are the metal induced gap states discussed above. Another feature evident in Region IV is the state at -8.5 eV denoted by S_K . This is an interface state whose charge density dies off in both directions of the interface, i.e., it is localized in the interface.

We have also computed the energy spectrum for a metal semiconductor interface using pseudopotentials for aluminum instead of the jellium model. Some

interesting features result, i.e., there appears to be a strong covalent type interaction between the aluminum atoms which exist even though the aluminum atoms are separated by four angstroms. This distance is considerably longer than that which occurs in bulk aluminum. The spectrum obtained agrees with recent experimental results.

* Partially supported by NSF

4. SURFACE STATES ON TRANSITION METALS USING PSEUDOPOTENTIALS*

M. L. Cohen, S. G. Louie, K. M. Ho and J. R. Chelikowsky

We have recently been able to extend our methods to calculate the surface electronic structure of a transition metal. Transition metals because of the d-electron contribution to states near the Fermi energy have been extremely important in surface physics. The role of these materials in catalysis is particularly interesting. We have performed the first self-consistent calculations for a transition metal; niobium was chosen as a prototype. Charge densities and local densities of states were calculated for states near the Fermi energy. A detailed description of these states and their relation to orbitals constructed from atomic wavefunctions was given. Since to our knowledge there is no published experimental data on the (001) surface of niobium, we have not yet been able to compare our results with experiment. Our results do illustrate the nature of the electronic wavefunctions for d-electrons near surfaces and we plan to concentrate on this area in the future. In particular we would like to extend our calculations to other transition metals.

* Partially supported by NSF

5. LOCALIZED-ORBITAL CALCULATIONS FOR BULK MATERIALS AND FOR ADSORBATES ON TRANSITION METALS*

M. L. Cohen and D. W. Bullett

A localized-orbital technique is used to calculate electronic structure of arsenic chalcogenides. The results are in good agreement with experiment and the method can be extended to consider random networks of As and chalcogen atoms. The method was also applied to examine the structural properties and valence force fields of Se and Te. In the latter case the total energy was obtained as a function of atomic positions and the energy minimum occurred within 5% of the observed bond length. The tendency toward a six-fold coordinated structure under pressure was demonstrated and the calculated valence force fields were in good agreement with experimental results.

The localized-orbital approach was also used to study the properties of H on W, H, O, and CO on Ni and Pt. As an example of the results obtained,

Fig. 3. Local density of states for the Al-Si interface. (XBL 771-7380)

the relative binding strengths of CO to various sites on Ni (100) and (111) surfaces were investigated. In the most stable configuration the CO molecule bonds through the C atom in a four-fold coordinated site on (100) and a d-fold site on (111). Calculated electronic energy levels of the chemisorbed gas are in good agreement with photoemission spectra.

* Partially supported by NSF

6. ELECTRONIC STRUCTURE OF SOLIDS AND MOLECULES*

M. L. Cohen, J. R. Chelikowsky, J. D. Joannopoulos, J. S-Y. Wang, K. M. Ho, S. G. Louie, M. Schlüter, P. Thiry, Y. Petroff and R. Pinchaux

Here we describe a variety of calculations connected with electronic structure. An exhaustive treatment of the electronic structure of 11 diamond and zincblende semiconductors was done using non-local pseudopotentials. In this work band structures, reflectivity spectra, electronic density of states and valence charge densities were presented and compared with experiment. Improved optical gaps, optical critical-point topologies, valence-band widths, and valence charge distributions are obtained as compared to previous local pseudopotential results. It is our opinion that the results for the 11 semiconductors represents the most accurate theoretical study of these materials. The materials are the most widely used semiconductors: Si, Ge, α -Sn, GaP, GaAs, GaSb, InP, InAs, InSb, ZnSe, and TdTe.

Other work related to the above group of semiconductors involves calculations of the valence charge densities in these materials and comparing these results with x-ray data. It is shown that nonlocal pseudopotential calculations give much better agreement with experiment than to local pseudopotential calculations. Another aspect which was investigated involves the role of electron-hole interactions of the d core-levels in III-V semiconductors. It is shown that photoemission and optical spectroscopy give different results for these materials and that one electron calculations fail to explain the experimental results. Electron-hole interactions and relaxation effects have to be included to explain the existing discrepancies.

Another application of the self-consistent pseudopotential method was made to case of Si₂ molecule. A calculation was done to estimate the bond length, the bond stretching force constant, and the binding energy of the molecule. The results were in fair agreement with experiment. Suggestions of how to use the pseudopotential method for more accurate molecular calculations were presented.

Because of our interest in dealing with d-electrons for surface calculations, we explored in more detail the application of the pseudopotential method to bulk material having d-electrons. One example was a calculation of the energy bands, densities of states, and charge densities for the noble metal compound AgCl.

Another calculation involved a self-consistent pseudopotential calculation of the electronic structure of niobium. The calculated band structure and density of states was in good agreement with APW calculations and with photoemission experiments. Our method allowed a computation of the electronic charge density and partial charge densities for specific energy regions. These calculations should give new insight into the electronic bonding of transition metals and perhaps even some information about vibrational spectra and superconductivity.

A detailed review was compiled to discuss the role of short range order and disorder in tetrahedrally bonded semiconductors. The review concentrated on modern methods developed in our group. Some of these methods were developed in collaboration with Professor Falicov's group. A detailed analysis of the methods to study short range order and short range disorder using complex crystalline models and cluster-Bethe lattice models was given. A compilation of the results was constructed.

* Partially supported by NSF.

7. OPTICAL PROPERTIES, BAND STRUCTURES AND BONDING OF LAYER COMPOUNDS

M. L. Cohen, M. Schlüter, J. Camassel, S. Kohn, J. P. Voitchovsky, Y. R. Shen, C. Y. Fong and D. W. Bullett

We have calculated the electronic structure of a variety of nontransition-metal layer compounds. These include GaSe, GaS, and alloys of these two materials, SnSe₂, SnS, PbI₂, and BiI₃. We have compared our results with a variety of experiments. In particular modulation spectroscopy experiments done in Professor Shen's group were analyzed using our theoretical results. We also used the results of our calculations to describe the valence band structure and chemical bonding for these materials. Our charge density and density of states calculations were used to explain the chemical nature of this series of materials.

8. SUPERCONDUCTIVITY -- PHONON AND NON-PHONON MECHANISMS*

M. L. Cohen and S. G. Louie

There has been considerable interest in recent years in the possibility of using the electronic polarizability of a semiconductor to induce Cooper pair formation and superconductivity in a thin metal layer on a semiconductor surface. This so-called excitonic mechanism of superconductivity has received attention both in the Soviet Union through the work of Ginzburg and in this country through the work of Allender, Bray, and Bardeen. The Allender, Bray, and Bardeen (ABB) work has been criticized by Inkson and Anderson (IA). IA use a model dielectric function for the semi-

conductor and metal to show that the net interaction between electrons in a metal-semiconductor geometry would be repulsive rather than attractive.

The results by Inkson and Anderson were reconsidered by our group using dielectric functions appropriate for the semiconductor and the metal. In particular the semiconductor dielectric function was based on a pseudopotential band structure of the semiconductor. The metal dielectric function was modeled using a Lindhard dielectric function. It was shown that the Inkson and Anderson models for the dielectric function were not consistent with the more realistic Lindhard model and the pseudopotential model. However, it was also shown that using the pseudopotential dielectric function the total interaction between the electrons in the semiconductor was in fact repulsive. This does not completely rule out the excitonic mechanism because umklapp contributions or local field contributions to the dielectric function are not included. These should be included before a definite statement about the excitonic mechanism can be made. It appears improbable at this stage that umklapp contributions will be large enough to yield a net attractive interaction but calculations with a complete nonlocal dielectric function have not been done.

Another aspect of our research in superconductivity is concerned with the calculation of the superconducting transition temperature, T_c , for arbitrarily strong electron phonon coupling parameter, λ . The solution of the Eliashberg equations is necessary to obtain T_c reliably. There are approximations to the solution of the Eliashberg equations and the most popular of these is the McMillan equation. The McMillan equation has been shown to yield incorrect values for T_c at large λ by Allen and Dynes. Recently there has been some controversy about the Allen-Dynes solution, and Leavens has raised the question of whether the Allen-Dynes solution is appropriate for specific electron-phonon interaction spectra.

To begin with we solved the Eliashberg equations in the Matsubara representation numerically and evaluated the superconducting transition temperature. Our results were consistent with those of Allen and Dynes and indeed demonstrated again the failure of the McMillan equation for strong electron-phonon coupling. We also were able to solve the Eliashberg equations analytically to obtain an approximate equation for the transition temperature. Using our numerical and analytic results we were able to show that the Allen-Dynes asymptotic limit for the transition temperature is in fact correct. The discrepancies pointed out by Leavens result from an imprecise definition of the condition for the asymptotic limit by Allen and Dynes. Except for this imprecise definition we have demonstrated that the results of Allen and Dynes are correct.

One of the most important by-products of our calculation is the new approximate equation for the superconducting transition temperature. This equation can be used to compute T_c for arbitrary coupling and removes the necessity of solving the complex Eliashberg equations. We have tested the

results for a wide variety of metals and alloys with excellent agreement between theory and experiment.

* Partially supported by NSF

9. RESEARCH PLANS FOR CALENDAR YEAR 1977

Marvin L. Cohen

We hope to extend our calculations on surfaces. In particular calculations of surface states for semiconductors will be performed. We would like to explore the (100) face of Si and also examine the properties of surface states on Ge and C. Interface calculations are also being planned. The metal-semiconductor interface using diamond has been a central problem in Schottky barrier research. We hope to attempt a calculation of this interface. Another interface problem which we hope to explore is the semiconductor-semiconductor interface. These heterojunctions have been studied recently by several experimental groups.

The most active research in surfaces will probably be concerned with transition metal surfaces. Our pseudopotential method is unique in that it is self-consistent and can be trusted to give reliable estimates of the energy spectra for surface states. The limitation of this method is that it requires a significant amount of computer time. We hope to develop new methods which will combine our pseudopotential approach with more localized orbital approaches to yield a tractable method applicable to a large variety of transition metal surfaces. Preliminary results indicate that this approach should work and yield reliable results. If the approach is flexible enough, it will also be applied to adsorbates on transition metal surfaces.

Some investigations of the feasibility of making total energy calculations for different geometrical configurations both in the bulk and on the surface of solids will be explored. Total energy calculations are difficult because they usually involve subtractions of large numbers with the hope of achieving accuracy in the differences between these numbers. We are not yet at a stage where we can reliably predict crystal structures but we feel that the calculations are sufficiently accurate that some attempts in this direction should be made at this time.

Further explorations using our approximate solution of the Eliashberg equations for the superconducting transition temperature will be explored. It is hoped that this equation can be applied to other problems in superconductivity. The role of umklapp processes or local field effects in exciton superconductivity will also be explored. This involves a difficult and long computation of the local field dielectric function. It is not clear at this time whether such a calculation can be done without the use of expensive computer time.

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C. MATERIALS CHEMISTRY

1. CHEMICAL STRUCTURE

a. High Pressure Chemistry

George Jura, Principal Investigator

1. HEAT CAPACITY DETERMINATION AS A FUNCTION OF TEMPERATURE AND PRESSURE

George Jura and Kwang Yul Kim

Excellent relative heat capacity measurements have been made as a function of temperature at various pressures using the microsecond pulse technique that has been developed in the previous years. In the past the difficulty with the technique has been working at constant temperature as a function of pressure. Instead of finding the heat capacity to decrease with increasing pressure, it is usually found that the heat capacity increases as the pressure is increased, a thermodynamic impossibility. (It is assumed that there are no electronic or polymorphic changes.)

Attention has been devoted to the solution of the apparent difficulty in the method. The electronics have been redesigned and rebuilt. There is on order a 12 bit AD convertor to increase the accuracy of the results which we now obtain. New amplifiers have been placed into service.

In the old apparatus, the first 180 microseconds were unusable because of the rise time for the pulse and the subsequent ringing. This has been reduced to approximately 40 microseconds.

The power capability has also been increased by a large factor. 4.5 amps was the maximum capability of the old equipment, 15 amps for the present. This means that there is a possible temperature increase of the sample of a factor of 10. This should yield considerably better results.

The new apparatus is in the testing state at the present time. It is hoped that our capability will be greatly increased.

We have also reexamined the theory behind the determinations. Originally, we assumed that for a period of time, the temperature of the surrounding medium could be considered to be constant. If this is a sufficiently accurate description of what occurs, we can write

$$dE/dt = [(I^2 R' - k)/C_p] E + kE_0/C_p \quad (1)$$

It is assumed that the current I is constant, E the voltage drop across the sample at time t . R' is dR/dT where R is the resistance of the sample and T the temperature. E_0 is the voltage at time zero, and k is the heat leak constant. This

equation can be integrated, and one finds after expanding the exponential in a power series,

$$E = E_0 + (AE_0 + B) \left[t + \frac{At^2}{2!} + \frac{A^2 t^3}{3!} + \dots \right] \quad (2)$$

where $A = I^2 R' - k$ and $B = kE_0/C_p$. Experimentally one finds that Eq. (1) describes the data from 200 to 1000 microseconds. Because of this agreement, we have not really examined the other possibility, namely that the temperature of the surroundings is a function of time. We have now done this.

In this treatment we assume that the wire is straight. Since the curvature is large compared to the diameter, no error will be introduced by this assumption. Second, it is assumed that the temperature gradient in the silver chloride extends from the surface of the wire to the carbide of the anvils, and that the temperature of the anvils is constant. Since the distance from the wire to the anvil faces is only 0.017 cm, it can be readily seen that the 0.5 cm distance to the air can be readily neglected. The final assumption that is made is that the wire is at a uniform temperature throughout its length and diameter. Using the previous assumptions and standard heat transfer equations, one finds that

$$E = E_0 + \frac{I^2 R_0 R'}{C_p} t - \frac{\kappa_2^{1/2} \alpha}{\Gamma(5/2)a} t^{3/2} + \frac{\kappa_2(2\alpha^2 - \alpha + 2\beta)}{4a^2} t^2 - \frac{\kappa_2^{3/2}(\delta\alpha^3 - \delta\alpha^2 + 16\alpha\beta - \alpha)}{\Gamma(7/2)8a^3} t^{5/2} + 0(t^3)$$

where

$$\alpha = \frac{A\kappa_2 a}{C_p \kappa_2} = \frac{A\alpha_2 C_{p2}}{C_{p1}}$$

$$\beta = \frac{I^2 R_0' a^2}{\kappa_2}$$

and

a: radius of a wire

$A=\pi a^2$: surface area of the wire

K_2 : thermal conductivity of AgCl

C_{p1} : bulk specific heat of the wire

κ_2 : thermal diffusivity of AgCl

$$\kappa_2 = \frac{K_2}{\rho_2 C_{p2}} .$$

ρ_2 : density of AgCl

C_{p2} : specific heat of AgCl

R_o^i : temperature coefficient of resistance

It is evident that if sufficiently good data could be obtained, that not only the heat capacity of the metal, but also the heat conductivity and the heat capacity of the surrounding material could be determined as well.

If the last equation is applied to the data, one marked improvement is observed, the heat capacity of the metal decreases with the pressure. However, the heat capacity is not a function of I^3 as required by the theory. If the earlier equations are used, the calculated heat capacity is a function of I^3 , but it gives the incorrect dependence of the heat capacity on the pressure.

It is hoped that when the necessary parts that will permit us to use the 12 bit AD convertor arrive that the above dilemma can be solved. It is now over 6 months that the convertor was ordered. It is three months that we have been waiting for a card for the PDP 8 so that use can be made of the convertor.

2. RESEARCH PLANS FOR CALENDAR YEAR 1977

George Jura

In 1977 it is expected that the rebuilding of the apparatus will be completed. Measurements will be made on a selected group of metals; iron, gadolinium, and bismuth to start. It is expected that the temperature range investigated will range from 77 to 298 K.

b. Low Temperature Properties of Solids

Norman E. Phillips, Principal Investigator

1. HEAT CAPACITY OF Tl-Pb-Bi ALLOYS

F. Hermans, J. Boyer, and Norman E. Phillips

The density of electronic states at the Fermi surface, $N(0)$, is of fundamental importance in determining many of the properties of metals including T_C , the critical temperature for superconductivity. In alloy systems the composition dependence of $N(0)$ has often been discussed in terms of the rigid-band model, in which it is assumed that the energy dependence of the density of states is the same for all alloys in the system and $N(0)$ varies with composition only through the changes in the Fermi energy that accompany changes in the number of conduction electrons. In recent years, however, it has been shown both theoretically and by photoelectron spectroscopy that this model is qualitatively incorrect. Although there is currently considerable interest in disordered systems,¹ very little quantitative data on $N(0)$ for alloys is available. In principle, it can be obtained for superconducting alloys from a combination of electron tunneling experiments, which give the electron-phonon interaction parameter λ , and heat capacity measurements, which give the coefficient of the electronic heat capacity, γ . These quantities determine $N(0)$ through the relation

$$\gamma = (2/3)\pi^2 k^2 (1+\lambda) N(0) \quad (1)$$

Although many alloy systems have been studied calorimetrically, only a very few of them have been the subject of electron tunneling measurements. Recently, tunneling data² for binary Tl-Pb and Pb-Bi alloys throughout the range of stability of the fcc phase and for a few of the ternary alloys have been reported. In this case it happens that the available heat capacity data³ are limited to binary alloys in a very narrow range of composition near pure Pb, and additional measurements are therefore of interest.

An additional incentive for obtaining $N(0)$ values for those superconducting alloys for which tunneling data are available is that they provide the additional information necessary to obtain separately each of the quantities that determine T_C . Extensions^{4,5} of the BCS theory⁶ to include strong-coupling effects and electron-electron repulsion give T_C as a function of λ and other quantities derivable from tunneling data. The definition of λ is

$$\lambda = \frac{N(0) \langle I^2 \rangle}{M \langle \omega^2 \rangle} \quad (2)$$

where $\langle I^2 \rangle$ is the average of the square of a matrix element for the scattering of an electron by a lattice vacancy, M is the atomic mass, and $\langle \omega^2 \rangle$ is a mean square phonon frequency. Tunneling data give both λ and $\langle \omega^2 \rangle$ so each factor on the right hand side of Eq. (2) can be evaluated if $N(0)$ is

known. This combination of data has not been available for alloy systems, but McMillan⁴ pointed out that for five pure transition metals the product $N(0) \langle I^2 \rangle$, both factors of which represent essentially electronic properties, is approximately constant, and λ and T_C are therefore largely determined by the vibration spectrum of the lattice. This observation led to a complete change in the interpretation of T_C data. Whereas formerly it was assumed that T_C was determined largely by electronic properties, it has become more usual to interpret the composition dependence of T_C in terms of McMillan's equation⁴ for $T_C(\lambda)$ and Eq. (2), with $N(0) \langle I^2 \rangle$ constant. Furthermore, since $\langle \omega^2 \rangle$ is often not available it is often replaced by the Debye temperature, Θ .

Normal-state heat capacity data and zero-field data near T_C have been obtained for binary alloys with conduction electron/atom ratio z ranging from 3.4 to 4.15, and for two "pseudo leads," ternary alloys of the form $\text{Pb}_{1-2x}\text{Tl}_x\text{Bi}_x$ with $x = 0.05, 0.10$. (After the heat capacity measurements were completed, the $z = 3.4$ and 3.6 alloys were discovered to be inhomogeneous. Those samples will be homogenized and remeasured, but the original results presumably give γ values that reflect an average over a range of composition centered at the nominal value and are included in this report.) In the analysis of the data the effect of phonon dispersion on the form of the lattice heat capacity and the hyperfine heat capacity were taken into account. Values of γ , Θ , and T_C were derived, and $N(0)$ was calculated from λ values obtained by interpolation from the published² data.

The results for both γ and $N(0)$, normalized to the values for pure Pb, are shown in Fig. 1. A striking feature of Fig. 1 is that although the slopes of γ vs. z are different for the Tl-Pb and Pb-Bi alloys, the values of $N(0)$ fall on a common straight line to within 0.5%, the apparent precision of the data. Furthermore, although the values of γ for $\text{Pb}_{0.9}\text{Tl}_{0.05}\text{Bi}_{0.05}$ and $\text{Pb}_{0.8}\text{Tl}_{0.1}\text{Bi}_{0.1}$ are 3.5 and 6.5% greater than for Pb, the values of $N(0)$ are all the same to within 0.5%. In these respects the results are consistent with the rigid-band model, but in light of what is now known about the electronic structure of alloys, that must be regarded as either a coincidence or indicative of some hitherto unrecognized correlation. Furthermore, the slope of $N(0)$ vs. z is not in agreement with that derived from band-structure calculations^{7,8} for Pb. (Earlier heat capacity data⁵ for $3.90 < z < 4.09$ were interpreted as being in agreement with the calculated Pb band structure and the rigid-band model. However, the γ values were of lower precision and the γ values used in the analysis were not in good agreement with the more recent results.)²

Fig. 1. The variation of γ and $\gamma/(1+\lambda)$ with z for the binary alloys. (XBL 7612-11010)

Smooth curves representing the z dependence of λ and its component factors are shown in Fig. 2. The curves are based on data reported by Dynes and Rowell² for λ and $\langle\omega^2\rangle^{-1}$; on data from Fig. 1 for $N(0)$; and on values derived from Eq. (2) for $\langle I^2 \rangle$. Throughout the range of z studied, $N(0)$ is essentially constant (except possibly for $z < 3.6$ where the data are suspect) and the trends with z of $\langle\omega^2\rangle$ and $\langle I^2 \rangle$ are in opposite directions. The net effects for the two alloy systems are quite different, however: for Pb-Bi alloys and increasing z , the strong increase in $\langle\omega^2\rangle^{-1}$ dominates the decrease in $\langle I^2 \rangle$ and produces the observed increase in λ ; for Tl-Pb alloys and $z > 3.8$ the two effects more nearly cancel and λ is essentially constant: for $z < 3.8$ the trends in $\langle I^2 \rangle$ and $N(0)$ dominate the behavior of λ . For Pb-Bi alloys, McMillan's correlation⁴ is approximately correct and the trend in λ is determined largely by changes in the phonon spectrum; for the Tl-Pb alloys on the other hand it is largely the electronic properties that determine λ . For the binary alloys, values of θ are compared with values of $\langle\omega^2\rangle^{1/2}$ derived from tunneling data² in Fig. 3. For $3.8 < z < 4.2$ the two quantities show very similar trends, supporting the commonly used practice of taking θ as a measure of $\langle\omega^2\rangle^{1/2}$ when more detailed information on the phonon spectrum is not available. For the pseudo leads ($\text{Pb}_{1-2x}\text{Tl}_x\text{Bi}_x$) there is a similar correspondence: Both θ and $\langle\omega^2\rangle^{1/2}$ show a marked decrease with increasing x . Presumably this behavior is related to the decrease in θ that is often observed when a pure metal is alloyed (as in the Tl-Pb and Pb-Bi alloys) and reflects a softening of the phonon

Fig. 2. Variation of λ and its component factors with z for the binary alloys. All quantities plotted are normalized to their values for Pb. (XBL 7612-11013)

Fig. 3. Comparison of θ and $\langle\omega^2\rangle^{1/2}$ for the binary alloys. Both quantities are normalized to the values for Pb. (XBL 7612-11015)

spectrum with increasing disorder. Since a characteristic phonon frequency appears as a pre-exponential factor in theoretical expressions for T_C , this softening produces a decrease in T_C . In the case of the pseudo leads, however, this decrease is more than offset by an increase in λ . Analysis based on Eq. (2) shows that the increase in λ is a consequence of a decrease in $\langle I^2 \rangle$ and a decrease, at twice the rate, in $\langle\omega^2\rangle$.

In summary, heat capacity data on fcc Tl-Pb-Bi alloys have been used with published values of λ to determine $N(O)$ and the other factors that contribute to the variation of T_C with composition. Qualitatively, the $N(O)$ values show a rigid-band type of behavior but the agreement is not quantitative and is presumably only coincidental. McMillan's correlation has been shown to be roughly correct for Pb-Bi alloys, but electronic properties are more important in determining T_C for Tl-Pb alloys. Data for the two ternary alloys studied show that the effects on T_C are a result of changes in both electronic and vibrational properties.

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2. IMPROVEMENTS AND EXTENSIONS OF THE LABORATORY TEMPERATURE SCALE

J. D. Boyer, Gary E. Brodale, William E. Fogle, Erwin W. Hornung, Brent S. Krusor, and Norman E. Phillips

a. General Description. Accurate temperature measurements are of critical importance for heat capacity measurements for several reasons. Since the value of the heat capacity depends on the measurement of a temperature difference, the accuracy is related to the derivative of errors in the temperature scale. In many cases it is one of several components of the total heat capacity that is of particular interest, and the separation of the various components is based on differences in their temperature dependences. Furthermore, the use of heat capacity data to test theoretical predictions often depends on the ability to distinguish between relatively small differences in temperature dependence. For these general reasons, and particularly because we are interested in extending our heat capacity measurements to lower temperatures, we have for the last several years put considerable effort into improving the accuracy of our temperature scale and extending it to lower temperatures.

Our current temperature scale, from 60 mK to 25 K, is based on two internationally accepted scales:¹ (1) T_{58} , which is defined in terms of ^4He vapor pressures, from 1 to 4.2 K (the ^4He vapor pressure scale, T_{62} , is intended to be identical with T_{58} in this region but can be established with greater precision) and (2) T_{68} ,

which is defined in terms of the resistance of platinum resistance thermometers, above about 20 K. We have actually used platinum thermometers calibrated on an older NBS scale, T_{55} , but the difference between these two scales is well characterized. (Both of these scales are defined to lower temperatures but the accuracy below about 16 K is highly questionable.) Between 4 and 20 K our scale is based on a series of gas thermometer measurements relative to a reference temperature near 20 K on T_{55} . At 4 K these measurements gave temperatures about 4 mK lower than T_{58} , but that discrepancy is within the uncertainty associated with the virial coefficients. A smooth interpolation between T_{58} and T_{55} was based on the gas thermometer data and on a germanium thermometer calibrated against the NBS acoustic scale,² which gives temperatures higher than T_{58} by about 10 mK at 4 K. Below 1 K the scale is based on an extrapolation of the susceptibility of single crystal CMN, $(\text{Ce}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O})$ which follows a Curie law³ to temperatures of the order of 10 mK. Throughout the range 60 mK to 25 K the scale is preserved on a number of germanium resistance thermometers, some of which are also used as working thermometers for heat capacity measurements.

The extension of the scale to below 60 mK is based on the establishment of temperatures in the 2 to 20 mK region by nuclear orientation (NO) thermometry. Germanium thermometers are not useful in this region. Single-crystal CMN thermometers used with conventional bridge techniques have heat capacities that are too large for working thermometers and thermal relaxation times that become too long even for primary thermometers below about 20 mK. We shall use small-sample susceptibility thermometers and SQUID (Superconducting Quantum Interference Device) circuitry⁴ for the susceptibility measurements both as working thermometers and for extrapolation of the scale to below the NO region. Nuclear susceptibility thermometers, e.g., Tl metal, can be expected to follow a Curie law in the region of interest and will be useful for the latter purpose, and also as working thermometers for measurements on metals with which they can be put in good thermal contact. Powdered CMN thermometers, after calibration against NO or Tl thermometers, will be useful for measurements on ^3He to about 1 or 2 mK, and diluted powdered CMN thermometers should be suitable for similar measurements to much lower temperatures. The application of powdered CMN thermometers to measurements on ^3He is somewhat special because the thermal equilibrium time of a ^3He -CMN mixture is unusually short: their application to measurements on other materials is limited by the equilibrium times in CMN-oil mixtures and they will probably not be useful below about 10 or 20 mK.

b. Recent Improvements in the Scale Above 60 mK. Several years ago a new series of ^4He vapor pressure measurements were made, and, because the possible sources of error are quite different, the vapor pressure of ^3He was also measured in the 1 to 2 K range. These measurements agreed to ± 1 mK, but gave temperatures about 2 mK lower than the earlier scale below about 2 K. At

the same time new susceptibility measurements on single crystal CMN were made which showed that an approximately constant 2 mK error in the older scale persisted to 0.3 K.

It has recently been suggested that superconducting critical temperatures be used as fixed points to check working temperature scales and the NBS supplies standard materials for this purpose.⁵ During the last year we obtained an NBS "fixed point" device containing Pb, In, Al, Zn, and Cd samples with $T_C \approx 7.2, 3.4, 1.2, 0.84$ and 0.52 K, respectively. The claimed accuracy of the T_C 's relative to T₅₈ or to the NBS acoustic scale varies from ± 1.5 mK to 2.5 mK and the reproducibility is of the order of a few tenths of a mK. For Pb, In, Al, Zn, and Cd, respectively, and allowing for the expected difference between T₅₈ and the NBS acoustic scale, we find T_C 's higher than those assigned by NBS by 0.2, -4.4, 2.6, 2.7, and 0.9 mK. We believe the accuracy of our combined vapor pressure and CMN thermometry in this region is ± 1 mK or better. The discrepancies are outside the combined estimated error limits for In and Zn, and significant compared with attainable accuracy in other measurements for all but Pb and Cd. Independent comparisons⁶ of a similar NBS fixed point device with ^3He and ^4He vapor pressures give T_C 's higher than the NBS values by 1.5 and 2.4 mK for Al and Zn, and suggest (although the comparison is based on an extrapolation) that T_C for In is 3.5 to 4 mK lower than the NBS value. In the same work T_C for Cd was found to be 0.3 mK lower than the NBS value, but this was also based on a slight extrapolation and is in a region in which ^3He vapor pressure thermometry is becoming inaccurate. Tentatively, we conclude that the NBS values of T_C are in error by more than their claimed accuracy for In and Zn, and that our observed values of T_C confirm our temperature scale at these five points to ± 1 mK.

In the past year we have also recompared the only two of the original set of germanium thermometers that are still in use. The data from several such comparisons over a 10-year period shows consistency to within a few parts in 10^4 in temperature.

c. Extension of the scale to below 60 mK. We have compared several powdered CMN-SQUID susceptibility thermometers with our established temperature scale above 60 mK, and also with a ^{60}Co in hcp Co NO thermometer at temperatures below 40 mK.

Since the NO thermometer requires a minimum of 20 minutes counting time for accurate temperature measurements, it is intended for use only as a primary thermometer. Although the usual practice⁷ in NO thermometry is to use a single detector we have found that using two detectors, one parallel and one perpendicular to the crystal axis, provides a valuable check. In our earliest measurements the two detectors gave temperatures differing by as much as 10%. The discrepancy was traced to slight errors in positioning the detectors and to drifts in gain. These problems have been reduced but not entirely eliminated, and the agreement between the two temperatures is within 2%. We expect that with further adjustment

of the counting equipment we can achieve 1% accuracy in temperature measurement.⁸

One powdered CMN thermometer uses 1 mg of CMN in a copper holder and the DC susceptibility is measured. Another thermometer uses 20 mg of CMN in an epoxy holder, thermal contact is made through silver wires, and the AC susceptibility is measured. Considerable improvements in thermal equilibrium times have been achieved and the sensitivity is as high as 0.3 μK even at temperatures as high as 20 mK. Both of these thermometers exhibit a T^{-1} susceptibility when compared with either the germanium thermometer or the NO thermometer but there is a discrepancy of several percent between the proportionality constants in the two regions. The reason for this discrepancy is not understood.

A thallium metal susceptibility thermometer has also been made, but not yet tested. Thermal contact is made by casting the thallium onto a silver wire, and provision for operation in variable fields to 400 Oe was made. The latter feature permits testing for the presence of electronic paramagnetic impurities. This thermometer is expected to have a usable sensitivity up to 0.1 K and to be useful as either a primary thermometer or a working thermometer to below 1 mK.

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3. THERMODYNAMIC PROPERTIES OF He II

Brent S. Krusor and Norman E. Phillips

a. Recalculation and analysis of earlier data for $T > 0.3\text{K}$. Some years ago apparatus was constructed for measurements of the constant-volume heat capacity, C_V , on ^4He at temperatures between 0.3 and 4.2 K and at moderate pressures. The apparatus incorporated a number of improvements over earlier apparatus for similar measurements, notably a valve that sealed that heat capacity cell (instead of using the "blocked capillary" technique) and provision for making heat capacity measurements to below 1 K without including the heat capacity of a cooling salt.

Although the apparatus was designed primarily for measurements on the solid phases, it was found suitable for measurements on the superfluid He II and was used to measure C_V of the superfluid from 4.2 K to temperatures low enough for extrapolation to 0 K. These measurements provided the first direct evidence that the phonon dispersion in He II is anomalous. The energy-momentum (e-p) relation for phonons is usually written

$$e = cp(1 - \gamma p^2 - \delta p^4 \dots), \quad (1)$$

where c is the low-frequency velocity of sound and γ and δ are constants. This leads to a phonon heat capacity of the form

$$C_{ph} = A_3(c)T^3 + A_5(c, \gamma)T^5 + \dots, \quad (2)$$

and the sign of A_5 is the same as that of γ . It is usually assumed that γ is positive, but the C_V data showed that A_5 was negative.¹ This result is of crucial importance for transport properties because the allowed phonon scattering processes depend on the sign of γ . It had not been discovered by other techniques because the relevant phonon frequencies were too high for conventional sound velocity measurements but too low for accurate data from inelastic neutron scattering.

Shortly after the measurements were completed but before the data on He II was completely analyzed, an error of approximately 2 mK in the laboratory temperature scale was discovered in the region between 0.3 and 2 K (see preceding article No. 2). The measurements in the solid and mixed-phase regions were approximately corrected to the new scale and have been published. Partly because the values of A_5 might be particularly sensitive to changes in the temperature scale, and partly because the other thermodynamic properties of He II had not yet been derived from C_V , it was decided to recalculate C_V for He II on the new scale before completing the analysis.

The low-temperature data have been refitted with the sum of C_{ph} and the Landau expression² for the roton heat capacity,

$$C_r = B \left[\left(\frac{\Delta}{kT} \right)^{3/2} + \left(\frac{\Delta}{kT} \right)^{1/2} + \frac{3}{4} \left(\frac{\Delta}{kT} \right)^{-1/2} \right] \exp \left(- \frac{\Delta}{kT} \right). \quad (3)$$

The resulting values for A_3 , A_5 and Δ/k are shown in Figs. 1-3. The recalculation has substantially reduced a troublesome discrepancy between the value of A_3 at the saturated vapor pressure ($v = 27.58 \text{ cm}^3/\text{mole}$) and sound velocity measurements. Formerly our value of A_3 was 2% lower than that calculated from sound velocities;³ the new value is 0.5% higher than that calculated from sound velocities, but suspected errors in the internationally accepted temperature scale, on which our data are based, could lower A_3 by up to 1%. The agreement therefore is within $\pm 0.5\%$. The qualitative form of Eq. (1) is not changed substantially by the recalculation but the magnitudes of A_5 and γ have been increased by about 20% at $V_m = 27.58 \text{ cm}^3/\text{mole}$. Several other experiments have now shown that γ is negative but

Fig. 1. The coefficient of the T^3 term in the phonon heat capacity as a function of molar volume for He II. (XBL 7612-11018)

Fig. 2. The coefficient of the T^5 term in the phonon heat capacity as a function of molar volume for He II. (XBL 7612-11017)

Fig. 3. The minimum energy in the roton spectrum as a function of molar volume. (XBL 7612-11016)

there is little agreement on its magnitude.⁴

Near T_λ the C_V data have been fitted by an expression of the form

$$C_\lambda = D + E \log |T - T_\lambda|. \quad (4)$$

For the purpose of deriving other thermodynamic properties it is very useful to have an analytical expression for C_V over the whole temperature range. This has been achieved with the expression

$$C_V = [C_{ph} + C_r] (1-f) + [C_\lambda + T^2 \{F(T^2 - T_\lambda^2) + G(T^4 - T_\lambda^4) + H(T^6 - T_\lambda^6)\}] f, \quad (5)$$

where $f = \exp[15(T_\lambda^{-1} - T^{-1})]$. With the values of the phonon and roton parameters determined by the low-temperature fit, the values of D and E determined by the fit in the region $T_\lambda - T < 10^{-2}$ K, and adjustable parameters F , G , and H , Eq. (5) represents the experimental data to within 2% over the whole range. Deviations from Eq. (5) were represented by a table of smoothed differences and the resulting representation of the C_V data has been used to calculate the entropy as a function of V and T from 0 K to T_λ .

b. Construction of apparatus for new measurements of C_V for He II. As noted above, there is now general agreement that the phonon dispersion in He II is anomalous⁴ but there is disagreement as to the magnitude of the coefficients γ and δ in Eq. (1) and even as to the correct form of Eq. (1). Since the frequencies at which the

anomalous dispersion occurs are inaccessible by the most direct measurements it is of interest to improve the accuracy with which the phonon dispersion curve is characterized by calorimetric data. Accordingly, we have rebuilt the cryostat in which the earlier data were taken to extend the measurements to lower temperatures and to reduce the heat capacity of the calorimeter.

The ³He evaporation refrigerator has been retained, but an adiabatic demagnetization stage consisting of chromium potassium alum potted onto copper wires with a casting resin has been added. The demagnetization stage is operated by a 17 kOe superconducting solenoid and is connected to both the ³He stage and the sample cell by superconducting thermal switches (also operated by superconducting solenoids). Temperatures below 60 mK, the lowest at which C_V will be measurable, are readily produced by this arrangement.

The old copper beryllium cell with integral valve has been replaced by an epoxy cell and a small metal valve. The advantage of the new arrangement is a greatly reduced low-temperature heat capacity. We estimate that the calorimeter and sample heat capacities will be of comparable magnitude near 0.1 K instead of near 0.35 K as in the old calorimeter. The cell itself is made from Stycast 1266, a room-temperature setting epoxy and contains two internally mounted electrical heaters. The metal valve was reduced substantially in mass because thermally it is part of the calorimeter, and its heat capacity is included in the measured heat capacity. It is connected to the cell by a copper capillary and to room-temperature by a copper-nickel capillary. It also carries the calibrated germanium thermometer and a capacitance-type strain gauge⁵ that will permit simultaneous measurements of $(\partial P/\partial T)_V$. The extreme small size of the valve necessitated elaborate precautions to prevent application of excessive torque to the screw that actuates the valve stem. A small spring is interposed between the valve stem and the actuating screw to produce the required relation between pressure on the valve stem and number of turns on the screw.

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4. RESEARCH PLANS FOR CALENDAR YEAR 1977

Norman E. Phillips and Associates

The $Tl_{0.6}Pb_{0.4}$ and $Tl_{0.8}Pb_{0.2}$ samples will be homogenized and remeasured. Additional work on this system -- extension to higher Tl and Bi concentrations and to ternary alloys with $z \neq 4$ -- may be undertaken.

The heat capacity of He II will be measured to below 0.1 K.

Measurements of heat capacities at low temperature and moderate pressure will be resumed. The first material to be studied is α -Ce, and arrangements to obtain a sample of the highest purity currently available have been made.

Additional work on powdered CMN-SQUID thermometers will be done in an attempt to resolve the discrepancies in our earlier measurements. The thallium-SQUID thermometer will be compared with NO thermometers using demagnetization of CMN from dilution refrigerator temperatures to reach temperatures below 5 mK. The thallium thermometer will then be compared with powdered CMN and powdered diluted CMN thermometers for use as working thermometers in measurements on ^3He . The first goal of the work on ^3He will be to obtain the heat capacity of the normal liquid as a function of temperature and pressure. The data will provide values of spin-fluctuation parameters that are important in determining superfluid

properties. In the same measurements we expect to get preliminary data on the properties of the superfluid phases and on CMN.

5. 1976 PUBLICATIONS AND REPORTS

Norman E. Phillips and Associates

Journals

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c. Mass and Charge Transport

Charles W. Tobias, Principal Investigator

1. FUNDAMENTAL STUDIES OF TRANSPORT PHENOMENA IN ELECTROCHEMICAL REACTORS

a. Studies of Events at Gas-Evolving Electrodes

Paul Sides and Charles W. Tobias

The dynamics of gas evolution at electrodes involve parallel and consecutive sequences of nucleation, bubble growth, coalescence, and separation from the surface into the electrolyte stream. Residence time and surface coverage determine effective current density, and hence, charge transfer overpotential, as well as the resistance offered to passage of charge in the electrolyte. A photographic study of incipient gas evolution allowed observation of surface events unobstructed by the rising bubble stream.¹ Surface coverage and coalescence during steady-

tool in opening up access to the elusive problem of modeling the gas evolution process.

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Fig. 1. Oxygen bubble growth photographed from behind $\text{SnO}_2\text{:Sb}$ surface with glass substrate. Current Density: 20 mA/cm^2
2N KOH electrolyte, 64 fps, 16 mm film. (XBB 773-1800)

state electrolysis are now being observed through transparent electrodes,² by using a Unitron overhead stage microscope focused through a glass substrate and a conductive oxide layer on the glass-electrolyte interface. A 2000 Å thick, smooth and transparent antimony doped tin oxide layer (conductivity: 0.015 ohm-cm) allows recording of bubble dynamics by still- and motion picture photography using a broad range of incident light angles.³ Initial studies employed oxygen evolution in 2 N KOH at up to 20 mA/cm^2 current density (Fig. 1). Nucleation occurred preferentially at artificial cavities and grooves, and coalescence events could be easily discerned. Average residence time was 0.17 second at 20 mA/cm^2 . Bubble size at separation, and contact areas with the $\text{SnO}_2\text{:Sb}$ substrate are clearly defined. Current work is aimed at the determination of surface coverage as a function of current density, flow rate, and electrode topology. The transparent electrode promises to be a powerful

b. Modeling of the Electrochemical Machining Process

James B. Riggs, Rolf H. Muller, and Charles W. Tobias

Although shaping of metals by high speed anodic dissolution has achieved considerable industrial importance, the cathode tool pieces are developed through costly trial and error procedures rather than on the basis of theoretical predictions. The effects of such process variables as current density, electrolyte properties, and flow rate are also established on an empirical basis.

While there are reports on modeling of the ECM process in the current literature,¹ these fail to take into account various elementary processes characteristically occurring in electrolysis under ECM conditions. To develop rational design and optimization procedures for ECM, a modeling effort

was undertaken in this laboratory¹ which takes into account the changing geometry of the moving boundaries in ECM under the influence of electric field, flowing electrolyte, current dependent overpotential, and current efficiency.

The model predicts the current distribution on a work piece by numerically solving the Laplace equation in the presence of current density dependent charge transfer overpotential at both cathode and anode surfaces. The conductivity of the electrolyte as it passes through the interelectrode gap is allowed to undergo changes due to rise in temperature caused by friction and ohmic dissipation, as well as due to increasing gas content. Instantaneous current distribution and local current efficiency are evaluated following suitably small time interwalls of current passage, and the anode profile is adjusted after each time increment by application of Faraday's law (i.e., by removing a metal layer corresponding to the distribution of current density on the work piece).

Experiments on hole sinking in copper and 302 stainless steel, using a modified commercial ECM apparatus, have been used to test the model.² Both transient and equilibrium (steady state) geometries were predicted with satisfactory accuracy. A model prediction and an experimental unsteady state profile which was obtained by terminating the dissolution process at a beginning stage of hole formation are compared in Fig. 2. Steady state hole geometry and model prediction are shown in Fig. 3.

Fig. 2. Comparison between model and experiment in ECM hole starting. Work piece: copper; Tool diameter: 0.728 inches; Feed rate: 24 mils/min; Depth of cut: 80 mils; Flow rate: 340 cm³/sec; Inlet pressure: 42 psig; Electrolyte: 2N KNO₃; Temperature at inlet: 24.5°C, at outlet: 27°C; Applied voltage: 13.4 volts; Current: 78 amperes. (XBL 7611-9763)

A computer generated motion picture was prepared showing in sequence (a) the surface memory effect upon the leveling of an initially sine-waved surface, b) the developing geometry in hole sinking, c) the response of a steady-state (equilibrium) geometry to a step-up of applied voltage, to a step-up in tool advance rate, and to an increase in electrolyte conductivity.

Fig. 3. Comparison between model and experiment in ECM equilibrium hole sinking. Work piece: 302 stainless steel; Tool diameter: 0.728 inches; Feed rate: 18 mils/minute; Flow rate: 400 cm³/sec; Inlet pressure: 30 psig; Electrolyte: 2N KNO₃; Inlet temperature: 24°C, at outlet: 27.5°C; Average valence of dissolution: 3.8; Applied voltage: 24.9 volts; Current: 122 amperes. (XBL 7611-9908)

1. R. H. Nilson and Y. G. Tsuei, Trans. ASME, March 1976, p. 54-58.
2. James B. Riggs, Rolf H. Muller, and Charles W. Tobias, Current Distribution in Electrochemical Machining, MMRD Annual Report for 1975, LBL-4550, p. 164.

2. RESEARCH LEADING TO NEW ELECTROLYSIS PROCESSES

a. Anodic Reactions in Propylene Carbonate - Aluminum Dissolution

Radoslav Atanasoski and Charles W. Tobias

The dissolution of aluminum could potentially serve as the anodic reaction in electrolysis cells in which the cathodic product is metallic potassium.¹ The anodic product, AlCl₃, a needed chemical, could be recovered as a solid precipitate from the saturated KAlCl₄ electrolyte. With this practical objective in mind, the following aspects of aluminum dissolution were investigated:

Apparent valency of dissolution was measured by weight loss of aluminum upon anodic dissolution at constant current in runs lasting over 200 hours. Results were confirmed by analysis of aluminum content of the electrolyte. Below 5 mA/cm² the valency is approximately 2.5 at 30°C, and 2.2 at 70°C. At higher current densities the apparent valency increases; at 20 mA/cm² it reaches 2.9.

The open circuit potential of the cell Al/0.5M KAlCl₄ in P.C./K was measured using different samples of 99.999% pure aluminum. Samples without treatment for removal of the oxide layer gave OCV-s in the range 2.4-2.8 volts,

those subjected to preelectrolysis: 2.2 ± 0.1 volt. Surfaces subjected to continuous renewal by scraping yielded OCV-s close to 1.9 volt. Surface amalgamation of aluminum resulted in a well reproducible OCV of 2.05 ± 0.05 volt. The most stable value, 1.875 ± 0.015 volt was obtained by using saturated aluminum amalgam.

Polarization Characteristics. Typical galvanostatic transients demonstrating the influence of the state of the surface on the overpotential are shown in Fig. 1. The maximum in the

Fig. 1. Galvanostatic transients for aluminum dissolution at 1, 2, 3, 4, and 5 mA/cm² (from the bottom); vert.: 0.2V/div, horiz.: 5 msec/div; potential before the pulses. 2.26 V vs. K/K⁺ in the same solution (0.5 M KAlCl₄ in propylene carbonate). (XBB 772-1354)

curves, after which higher activity state is evident, indicates the presence of passivation phenomena. In steady-state measurements this behavior has resulted in a more negative potential at higher current densities (e.g., 2.4 volt at 15 mA/cm² as compared to 2.8 volt at 1 mA/cm²). All evidence points to that aluminum reacts with the solvent, at least to the degree of forming a surface compound, which however doesn't cause passivity as in, e.g., aqueous solutions.

1. C. W. Tobias and J. Jorne, Method of Production of Alkali Metals and their Alloys, U.S. Patent No. 3,791,945. Assigned to the USAEC, 1973.

b. Hybrid Electrochemical-Thermochemical Cycles for the Production of Hydrogen from Water

David H. Munger and Charles W. Tobias

Water decomposition cycles, of the hybrid type, involving an electrochemical cell producing hydrogen and an oxide, and a subsequent thermochemical process loop which liberates oxygen and regenerates the lower oxide (or metal), are evaluated.¹ For example, a cycle based on the oxides of lead would involve:

In principle, such cycles would allow the positive characteristics of conventional water electrolysis and those of thermochemical water-splitting cycles to be exploited to give higher energy efficiencies. Calculated efficiencies of 28% to 46% for the hybrid cycles compare favorably to the 20% to 25% range for conventional water electrolysis. The reasons for this proposed higher efficiency are: low reversible cell voltages required, lower level of irreversibilities incurred during electrolysis because of lower ohmic losses and a more reversible electrode reaction replacing the oxygen electrode, and efficient thermal decomposition.

The hybrid processes in principle offer comparable energy efficiencies to thermochemical cycles. Less difficult separation steps and fewer corrosion problems may represent additional advantages.

Among the major problems of hybrid processes are: high solubility of the anodic reactant (or product), incomplete thermal reactions, difficult material handling, poor heat exchange characteristics, and difficult filtration due to degradation of the solid material. The technological feasibility and economic promise of the hybrid processes considered are judged not to be sufficient to contemplate their practical implementation.

1. David H. Munger, A Preliminary Evaluation of Hybrid Electrochemical Cycles for the Production of Hydrogen from Water, (M.S. thesis, University of California, Berkeley) LBL-5477, August 1976.

3. RESEARCH PLANS FOR CALENDAR YEAR 1977

Charles W. Tobias

(a) Investigation of the Dynamics of Gas Evolution. Transparent SnO₂:Sb electrodes will be used to observe and record bubble nucleation, growth, coalescence and separation phenomena. The dependence of residence time and of surface coverage on process variables will be evaluated. Impedance measurements will be employed for determining the incremental resistance caused by the first layer of bubbles.

(b) Mass Transport and Current Distribution in Electroforming. The model developed in this laboratory for the simulation of developing anode geometry in electrochemical machining will be adapted for high speed metal deposition processes (electroforming). An experimental program will be initiated for the study of mass transport limitations in the electroforming of complex shaped objects.

(c) Anodic Reactions in the Propylene Carbonate-KAlCl₄ System. The aluminum anode as a sacrificial electrode in potassium recovery from propylene carbonate solutions will be further evaluated. Other alternatives for anodic reactions to be considered will include liberation of a halogen, formation of an insoluble halide, and application of a diaphragm (Nafion) to allow use of two different solvents for the cathode and anode reactions.

4. 1976 PUBLICATIONS AND REPORTS

Charles W. Tobias and Associates

Journals

1. F. R. McLarnon, R. H. Muller, and C. W. Tobias, Interferometric Study of Transient Diffusion Layers, *Electrochimica Acta* 21, 101 (1976).

Papers Presented and Invited Lectures

1. R. A. Putt and C. W. Tobias, A Photographic Study of Incipient Gas Evolution, 149th Meeting of the Electrochemical Society, Washington, D. C., May 2-7, 1976.
2. R. E. Acosta, R. H. Muller, and C. W. Tobias, Mass Transfer Under Conditions of High Rate Electrolysis, 149th Meeting of the Electrochemical Society, Washington, D.C., May 2-7, 1976.
3. U. Landau and C. W. Tobias, Mass Transport and Current Distribution in Channel Type Electrolyzers in the Laminar and Turbulent Flow Regimes, 149th Meeting of the Electrochemical Society, Washington, D.C., May 2-7, 1976.
4. C. W. Tobias, Application of Electrochemical Engineering Principles to Energy Conservation

Problems, Workshop on Energy Conservation in Industrial Electrochemical Processes, Sponsored by ANL, BNL and ERDA, Argonne National Laboratory, August 10-12, 1976.

5. R. E. Acosta, R. H. Muller, and C. W. Tobias, Transport Processes in High Rate Electrolysis, 82nd National Meeting of the AIChE, Atlantic City, N.J., August 29- September 1, 1976.

6. C. W. Tobias, An Assessment of the Role of Electrochemical Engineering in Energy Conservation, Federal Institute of Technology, Zurich, Switzerland, September 3, 1976.

7. C. W. Tobias, Current Distribution on Advancing and Receding Electrode Surfaces, Keynote Lecture, 27th Meeting of the International Society of Electrochemistry, Zurich, Switzerland, September 6-11, 1976.

8. C. W. Tobias, Instantaneous and Transient Current Distributions, 150th Meeting of the Electrochemical Society, Las Vegas, Nevada, October 17-22, 1976.

9. C. W. Tobias, Advances in Electrochemical Engineering, Lead-off Address in the Symposium on Highlights of Applied and Basic Research on Electrochemical Cells, Stanford University, December 9-10, 1976.

LBL Reports

1. Uziel Landau, Distribution of Mass Transport Rates Along Parallel Plane Electrodes in Forced Convection, (Ph.D. thesis, University of California, Berkeley), LBL-2702, January 1976.
2. David H. Munger, A Preliminary Evaluation of Hybrid Electrochemical-Thermochemical Cycles for the Production of Hydrogen from Water (M.S. thesis, University of California, Berkeley), LBL-5477, August 1976.

2. HIGH TEMPERATURE AND SURFACE CHEMISTRY

a. High Temperature Chemistry

Leo Brewer, Principal Investigator

1. HARD SPHERE CALCULATIONS OF SOLUBILITIES IN LIQUID METALS

R. H. Lamoreaux

A method for estimating noble gas solubilities in liquid metals has been developed. Equations have been derived for predicting integral and partial molal excess entropies of mixing of liquid metals in the hard-sphere approximation. These excess entropies are being used to refine regular solution predictions of the solubilities of refractory metals in the liquid metals used as heat transfer media.

2. DIFFUSION IN MOLYBDENUM*

R. H. Lamoreaux

An exhaustive compilation of data on diffusion in molybdenum, its compounds, and its alloys has been completed for publication in 1977 in the Atomic Energy Review, special issue on molybdenum, physico-chemical properties of its compounds and alloys.

3. THERMODYNAMICS AND PHASE DIAGRAMS OF THE BINARY SYSTEMS OF MOLYBDENUM†

L. Brewer

Chemical bonding models have been used to evaluate the thermodynamic properties of the binary systems of molybdenum with each of the elements from hydrogen to lawrencium and the thermodynamic values have been used to calculate the phase diagrams of one hundred binary systems. This material will be published in 1977 in the Atomic Energy Review, special issue on molybdenum, physico-chemical properties of its compounds and alloys.

4. HIGH-TEMPERATURE SOLID-ELECTROLYTE CELL MEASUREMENTS OF THE THERMODYNAMIC PROPERTIES OF ALLOYS OF TANTALUM AND IRIDIUM

G. Bullard and D. Goodman

Solid solutions of ZrO_2 and CaO and of HfO_2 and ThO_2 with Y_2O_3 are being used as high-temperature electrolytes in high-temperature cells for measuring the variation of the Gibbs energy

with concentration in systems with strong generalized-Lewis-Acid-Base interactions. These data should improve the use of chemical bonding models for prediction of thermodynamic properties of metal alloys.

*Supported by the International Atomic Energy Agency, Vienna.

†Supported in part by the International Atomic Energy Agency, Vienna.

5. MATRIX ISOLATION SPECTRA

Walter Duley, Lester Andrews, and Beat Meyer

Work on the reactions of calcium atoms with various oxygen compounds has been completed and the final manuscript will be submitted for publication shortly. Work in the future will be mainly directed toward study of metal clusters.

6. RESEARCH PLANS FOR CALENDAR YEAR 1977

Leo Brewer

During 1977 the use of the high-temperature solid electrolyte cell technique will be expanded to explore strongly interacting metallic systems in which one metal does not have enough electrons to utilize its low-lying electronic orbitals, and, therefore, can act as a generalized-Lewis-Acid, and one metal has so many electrons that the low-lying orbitals are occupied by nonbonding pairs of electrons. These types of interactions have a profound effect upon the thermodynamics of metal systems, and have been responsible for unexpected reactions between metals and refractories in automobile exhaust catalysts, nuclear power space capsules, and a variety of high-temperature systems in which platinum group metals are in contact with compounds of metals of the left side of the transition series. Matrix studies will be designed for a detailed examination of the interaction of atoms in pairs, triatomics, and larger clusters using UV and IR spectral studies to study the diffusion and reaction of the atoms to form the clusters and to characterize the properties of the products formed. Possibly additional compilations of thermodynamic data and phase diagrams of additional metal systems will follow the molybdenum work.

7. 1976 PUBLICATIONS AND REPORTS

Leo Brewer and Associates

Journals

1. Leo Brewer, Proceedings of the 4th Calphad Meeting, 1975 (Publ. 1976), pp. 38-45, 54-58, 73-76.
2. Beat Meyer, Elemental Sulfur, Chem. Rev. 76, 367 (1976).
3. Beat Meyer, The Structures of Elemental Sulfur, Adv. Inorg. Chem. Radiochem. 18, 287 (1976).
4. Lester Andrews, Ultraviolet Absorption Studies of the Alkali Metal Atom-Oxygen Molecule Matrix Reaction, J. Mol. Spect. 61, 337 (1976).
5. Lester Andrews, Optical Spectra of the Dibromide and Diiodide Ions in the Matrix-Isolated $M^+Br_2^-$ and $M^+I_2^-$ Species, J. of Amer. Chem. Soc. 98, 2152 (1976).
6. Lester Andrews, Optical Spectra of the Difluoride and Dichloride and Trichloride Ions in the Matrix-Isolated $M^+F_2^-$, $M^+Cl_2^-$, and $M^+Cl_3^-$ Species, J. of Amer. Chem. Soc. 98, 2147 (1976).

LBL Reports

1. Robert H. Lamoreaux, Melting Point Gram-Atomic Volumes and Enthalpies of Atomization for Liquid Elements, LBL-4995.
2. Robert H. Lamoreaux, Chapter 4, Diffusion, submitted to the Atomic Energy Review, LBL-5115.
3. Robert H. Lamoreaux, Estimation of the Solubilities of the Noble Gases in Liquid Metals: Programs for the HP-65 Calculator and Computational Details, LBL-5158.
4. Robert H. Lamoreaux, Estimation of the Solubilities of the Noble Gases in Liquid Metals, LBL-5159.

Invited Lectures

1. Leo Brewer, Plenary Lecture at the National Bureau of Standards. Conference on Vistas in Chemical Thermodynamics and Energy Problems on July 23, 1976.
2. Leo Brewer, Seminar on Transition Metal Alloys of Extraordinary Stability for an ERDA Group at Germantown, April 28, 1976.

b. Nuclear Technology Problems

Donald R. Olander, Principal Investigator

1. LIMITATIONS OF THE MODULATED MOLECULAR BEAM-MASS SPECTROMETRIC TECHNIQUE IN STUDYING GAS-SOLID REACTIONS*

D. R. Olander

The study of gas-solid chemical reactions involves a combination of modulated molecular beams, high vacuum, mass spectrometry, and phase-lock or digital processing techniques. Both the inherent advantages and the limitations of the molecular beam method lie in the way in which the reactant gas is delivered to the target. A molecular (or atomic) beam is a narrow, nearly parallel ray of particles moving in straight lines at the velocities imparted to them by the flow through the source. The primary beam molecules collide with nothing (including each other) until they strike the solid reactant. The reactant delivery system permits control of the angle at which the molecules strike the surface, a property which has been exploited in chemisorption studies. The collimated nature of the incident beam makes it possible to study particular crystallographic faces of the target solid, that, in some instances, reveals spectracular differences in reactivity.

Similarly, the products desorbing from the surface are detected in collision-free flight, that avoids quenching errors inherent in conventional sampling of hot reactive gases. Collisionless sampling also permits free radical reaction intermediates to be detected should they be emitted from the solid surface.

The collimated nature of the incident reactant gas beam has also provided the experimentalist with a new means of exploiting isotope exchange as a technique of unraveling surface processes. In addition to the common technique of utilizing mixtures of enriched isotopes as reactants, one isotope may be contained in the modulated reactant beam and the other caused to impinge on the surface from a nonmodulated source. The latter method was applied to the interaction of water vapor with graphite and of hydrogen on Pt.

Several of the obvious limitations of the molecular beam method are not especially critical; the reaction product must be volatile. For example one cannot study the corrosion of iron by oxidizing gases by this method. The reactants and products must all have different masses to be differentiated by the mass spectrometer detector. This restriction effectively precludes study of isomerization reactions and reactions which produce species of the same mass (for example, N_2O and CO_2 or CH_4 and O).

There are, however, more fundamental reasons why the molecular beam method is limited in its scope. The principal limit is in the nature of the molecular beam reactant itself. The strength of the primary molecular beam impinging on the solid reactant is limited by the available pumping speed and geometrical constraints of the apparatus.

Most experiments produce primary beams that have an intensity of $\sim 10^{14}$ molecules/cm²-sec striking the target. This impingement rate corresponds to a random gas pressure of $\sim 10^{-7}$ Torr. The highest reactant beam intensities which have been used in surface chemical studies approach 10^{-4} Torr equivalent pressure. High primary beam intensities are attainable only by making the distance between the source and the target and between the target and the mass spectrometer as small as possible (because the beam intensity decreases as the inverse square of the distance traveled). Given the necessity for a mechanical chopper, vacuum walls with collimators for differential pumping, and a reasonable flow area for exhausting the gas load, flight paths less than a few centimeters do not appear to be feasible.

Since gas-solid reactions of commercial interest are carried out at pressures about seven orders of magnitude higher than those characteristic of molecular beam experiments, the benefits of the modulated beam method are generally not translatable to chemical systems of technological interest. An extrapolation of a reaction mechanism determined by a low-pressure molecular beam experiment by a factor of 10^7 in reactant gas pressure is justifiably viewed with some suspicion by those interested in the application of gas-solid kinetics to practical situations. However, problems generated in newly developed technologies, including space vehicle reentry into the upper atmosphere and chemical attack of fusion reactor structures by the confined plasma, can directly benefit from the detailed sort of low-pressure chemical kinetic data which the molecular beam method is well suited to provide.

Because of the inherently transient (although periodic) and spatially collimated character of the reactant gas supply to the surface, modulated beam experiments are often considerably complicated by long-range diffusional processes on the surface or in the bulk of the solid target. These transport processes, although interesting in their own right, must be properly identified and accounted for in data analysis if an accurate picture of the surface chemistry is to be had.

Short-range diffusional processes, usually involving migration of species over the solid surface to reactive sites, have been uncovered in many modulated beam chemical studies. In contrast to long-range diffusion, short-range migrational steps of this type represent integral parts of the surface chemistry and are not merely experimental artifacts of the molecular beam method. It is to the credit of this technique that it is the only one which has thus far been capable of elucidating the fundamental importance of surface transport in many gas-solid reactions. These steps are made visible in modulated molecular beam experiments only by virtue of phase lag information; surface migration to active sites produces no new products nor does it affect the

steady-state reaction rate; it simply introduces a time lag in the release of products which could not possibly be detected by any steady-state experiment.

* Paper to be published in Adv. in Colloid and Interface Science.

2. INVESTIGATION OF THE TANTALUM-FLUORINE REACTION BY MODULATED MOLECULAR BEAM MASS SPECTROMETRY*

A. Machiels[†] and D. R. Olander

The reaction of molecular fluorine with polycrystalline tantalum was studied by modulated molecular beam-mass spectrometric methods. The apparatus was described in the 1974 Annual Report. The reaction was investigated at temperatures of 690 and 930°K at equivalent fluorine pressures between 10^{-5} and 10^{-4} Torr. TaF_5 was identified as the sole reaction product. Lower fluorides of tantalum were not present in the product vapors. Fluorine atoms could not be detected, but on theoretical grounds were not expected. Figure 1 shows the waveforms obtained by pulse counting the mass spectrometer output signal and digital data processing. The F_2^+ signal represents the temporal shape of the incident fluorine reactant beam, and the waveform labeled TaF_4^+ corresponds to the reaction product TaF_5 . These waveforms are treated to extract their fundamental

Fig. 1. Waveforms of the reactant F_2 and product TaF_5 obtained in the study of the Ta/F_2 reaction, 690°K surface, room temperature beam 1×10^{15} molecules/cm²-sec, modulation frequency 10 Hz, counting times F_2^+ - 5 min., TaF_4^+ - 30 min. (XBL 767-7198)

modes; kinetic information is contained in the ratio of the amplitudes of the fundamental modes of F_2^+ and TaF_4^+ and their phase difference.

The molecular beam data support a reaction model involving a thin scale of a lower fluoride (probably TaF_3) present on the surface during reaction. The model is presented pictorially in Fig. 2 and corresponds to the following sequence of elementary steps:

Reaction (1) represents the dissociative chemisorption of molecular fluorine on the upper surface of the TaF_3 scale. The sticking probability controlling this step is coverage dependent. Reaction (2) represents the production of TaF_5 by the reaction between adsorbed F atoms and the TaF_3 scale. This reaction is considered to be slow (i.e., with a characteristic time of the same magnitude as the modulation period) but irreversible. Reactions (3)-(5) provide a

Fig. 2. Schematic of model of the Ta/F_2 reaction. (XBL 7610-9347)

mechanism for regenerating the TaF_3 scale that is consumed at its upper surface of the scale with a solubility coefficient H [step (3)], then diffuse through the scale to the metal-scale interface [step (4)], where they rapidly and irreversibly react to form TaF_3 [step (5)].

Table 1 lists the parameters of the reaction model deduced from the data.

Table 1. Constants of the scale model of the Ta/F_2 reaction.

$T, ^\circ\text{K}$	η_0	$N_s, \text{sites}/\text{cm}^2$	H^2D, sec^{-1}	$k_R, \text{cm}^2/\text{sec}$
690	0.30	5×10^{14}	140	7.4×10^{-14}
930	0.42	8×10^{14}	25	7.9×10^{-14}

The bare surface sticking probability (which refers to F_2 on TaF_3) is large and slightly temperature-dependent. The magnitude of η_0 is consistent with the very high reactivity of fluorine with refractory metals found by others. However, the Ta/F_2 system appears to be unique in the ability of the reaction to proceed even in the presence of a lower fluoride scale. The site density N_s obtained from the data for each temperature is very close to the density of atoms on a solid surface. This implies that special surface sites are not needed for F_2 dissociative chemisorption on TaF_3 ; the entire surface is active provided it is not blocked by adsorbed F atoms.

The bulk solution/diffusion parameter H^2D contains two individual temperature-dependent quantities: the solubility H and the diffusion coefficient D . It appears from Table 1 that the solubility decreases with temperature more rapidly than the diffusion coefficient increases, resulting in a negative activation energy for the product H^2D .

The rate constant for the surface reaction, k_R , is seen from Table 1 to be temperature-independent. Even though the data suggested that reaction (2) was of order 2 with respect to $\text{F}(\text{ads})$, the observed zero activation energy of k_R is not expected for an elementary surface reaction. Rather, reaction (2) is probably a composite of several elementary steps which fortuitously has a zero net activation energy. In the reaction model, the kinetics are governed by the diffusional properties and the reactivity of the lower fluoride scale with respect to adsorbed F atoms. No independent evidence of a surface scale was obtained, however.

* To be published in Surface Science.

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3. MODULATED MOLECULAR BEAM STUDY OF THE PLATINUM-CATALYZED HYDROGEN GRAPHITE REACTION

M. Balooch,[†] R. Behrens and D. R. Olander

Recently it has been shown that formation of methane and acetylene from the hydrogen-graphite reaction requires that the reactant hydrogen be present in its atomic form.¹ Since platinum is known to dissociate H_2 into hydrogen atoms,² a study of the formation of methane from the reaction of H_2 with graphite surfaces covered with small amounts of platinum is currently under way. Preliminary results indicate that platinum does catalyze the H_2 -graphite reaction but with a smaller apparent reaction probability for methane production than found for the H-graphite reactions. Other salient features from our initial results are: (a) a reversal of the relative activity of the two orientations of graphite with larger reaction probability for the basal plane than for the prism plane; (b) a phase lag dependence on the H_2 beam intensity which is indicative of a nonlinear reaction mechanism; (c) a maximum in the methane production probability occurs when the quantity of deposited platinum is varied. Too little platinum provides insufficient dissociative area for the incident H_2 and too much platinum blocks the graphite surface and prevents access of the adsorbed H-atoms to the carbon.

Further experiments are being performed to add to our initial results. A model taking into account surface diffusion of hydrogen atoms from the platinum to the graphite surface is being developed to analyze this reaction.

[†]Current address is Department of Mechanical Engineering, Arya Mehr University, Teheran, Iran.

1. M. Balooch and D. R. Olander, J. Chem. Phys. **63**, 4772 (1975).

2. S. L. Bernasek and G. A. Somorjai, J. Chem. Phys. **62**, 3149 (1975).

4. THE INTERACTION OF WATER VAPOR AND PYROLYTIC GRAPHITE

A. Ullman* and D. R. Olander

Preliminary data pertinent to the kinetics and mechanism of the isotope exchange reaction:

and the chemical reaction:

were reported in the 1973 and 1974 Annual Reports. Final results and data interpretation are summarized here.

Both isotope exchange and chemical corrosion are dominated by the diffusional transport of

reactants and products in the bulk of the graphite. Gaseous reactants impinging on the surface adsorb with a high and temperature-independent sticking probability of about 15%. The adsorbed species migrate rapidly over the surface to grain boundaries where solution in the solid occurs. The adsorbed water species migrate along the high diffusivity paths afforded by the grain boundary and also at a slower rate in the grains proper. This "double diffusion" phenomenon is manifested experimentally by a very sluggish change in the reaction product phase lag as the modulation frequency is varied.

Figure 1 shows this behavior for the isotope exchange reaction, where a steady D_2O beam and a modulated H_2O beam acted as reactants and HDO was the sole reaction product. The theoretical curves on this figure are based on the following mechanism: (a) simultaneous grain boundary and lattice diffusion of all isotopic species in the solid, (b) isotopic equilibrium of reaction (1) at all locations within the solid, and (c) desorption from the surface to the gas phase.

Fig. 1. HDO reaction probability ϵ_{HDO} and phase lag ϕ_{HDO} for water vapor isotope exchange on graphite. (XBL 743-5679)

Fig. 2. Reaction product reaction probabilities and phase lags. (XBL 733-5846)

The double diffusion aspect of the model is responsible for the nearly constant phase lag over four orders of magnitude variation in modulation frequency. The rapid rise in the HDO phase lag at high frequencies arises because the modulation time becomes comparable to the mean desorption residence time of HDO on the surface. Another significant aspect of the isotope exchange data is the insensitivity to temperature; the isotope exchange process is as active at 300°K as at 1800°K.

In order to study the chemical reaction of water vapor and graphite, only a modulated H_2O reactant beam was used. Both CO and H_2 reaction product species were detected, in approximately equal quantities as indicated by the stoichiometry of reaction (2). The effect of frequency on the apparent reaction probability and phase lag is shown in Fig. 2. Curves representing the HDO data from Fig. 1 are also shown in Fig. 2. The reaction probability for CO and H_2 production are between one and two orders of magnitude smaller than the sticking probability inferred from the isotope exchange experiments. Graphite is very resistant to attack by H_2O ; no reaction was detected below 1800°K, but thereafter corrosion increased rapidly with temperature. The CO phase lag data shown in Fig. 2 are consistent with a mechanism of double diffusion of both the H_2O reactant and the CO product (i.e., the CO reaction phase lag is roughly twice as large as the HDO isotope exchange phase lag at all frequencies). The H_2 reaction product does not show the same influence of bulk migration processes as does the CO, as would be expected for the more mobile nature of the smaller species.

The overall picture of the graphite-water vapor interaction may be summarized as follows: the sticking probability of water vapor on clean graphite is high (~ 0.15) at all temperatures. From room temperature to $\sim 1800^\circ K$, the water molecules sorbed in and on the graphite are subject to bond-breaking and reformation. This process is responsible for the isotope exchange properties of graphite. At temperatures in excess of 1800°K, dissociation of H_2O is no longer automatically followed by reconstitution of the water molecule; as the temperature is increased, the probability of abstraction of carbon atoms by the dissociated water to produce CO and H_2 becomes ever more significant.

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5. LASER VAPORIZATION OF UO_2 *

H. C. Tsai, A. Covington[†] and D. R. Olander

One of the uncertainties in the prediction of the course of events in a reactor accident (such as a LOCA) is the knowledge of the vapor pressure of UO_2 at temperatures in excess of 3000 K. The vapor pressure controls the rate of mass loss from the molten fuel and hence determines such

phenomena as aerosol dispersion of the heavy metals, and in a fast breeder, the possibility of nuclear recriticality. Understanding the nature of the vaporization process can help to explain the thermochemistry of the binary oxide at high temperatures. In addition, there is the question of whether the vaporization rate in a rapid thermal transient (μsec or msec duration) can be treated by equilibrium models (e.g., by the Hertz-Langmuir equation).

The most convenient heat source for triggering the temperature transient in the refractory solid is pulse laser irradiation. The rapid heating produces a pulse of vapor which can be detected either by photographing the vapor plume that develops when a background gas is present or, in vacuum, by mass spectrometric identification of the vaporizing species.

Fig. 1. Vapor plume generated by laser pulse on UO_2 . Peak power density = $3.5 \times 10^5 \text{ W/cm}^2$; background gas pressure = 25 Torr; crater diameter = 2.9 mm; maximum apparent surface temperature = 4480K. (XBB 773-1850)

Fig. 2. UO_2 vapor pressure measurements. (XBL 773-5195)

When a background gas is present, the vapor pulse shows many of the characteristics of free-jet expansion. Figure 1 shows the barrel shock and Mach disk typical of this type of aerodynamic flow. The distance of the Mach disk from the surface is simply related to the vapor pressure of the solid at the maximum temperature attained during the laser pulse. Temperatures are measured by a fast pyrometer. The vapor pressures determined by this method are shown in Fig. 2 and compared with extrapolations of low temperature measurements obtained by conventional vapor pressure methods. The discrepancy at $T > 3500\text{K}$ is believed to be due to nonequilibrium radiation from the hot UO_2 vapor in the plume, which is apparently very rich in excited species emitted from the surface. Correct surface temperatures can best be determined by calculation based upon the laser energy input. The calculation is adjusted to give agreement with the pyrometer measurement at $\sim 3300\text{K}$.

* Joint project with NASA Ames Research Center.

† Research scientist, NASA Ames Research Center.

6. HOMOGENIZATION OF MIXED OXIDE FUELS*

D. R. Olander

$(\text{U},\text{Pu})\text{O}_2$ fuels for plutonium recycle in light water reactors or for LMFBR's are usually prepared from mechanically blended powders of the two pure oxides. Sintering conditions of 1600-1700°C in hydrogen gas provide acceptable porosity reduction and O/M control but are not sufficient to produce heavy metal mixing on an atomic scale. One possible method of promoting atomic dispersion of the heavy metals in a mixed oxide (other than by using feed prepared by co-precipitation) is by annealing the sintered pellets at sufficiently high temperature that intimate mixing is achieved by interdiffusion of plutonium and uranium cations. Classical diffusion theory was employed to assess the kinetics of the homogenization process.

The extent of homogenization can be characterized by the ratio of the maximum to the average plutonium concentrations (q_0/q_{av}), which occurs at the center of the original PuO_2 particle. Of practical interest is the time required for the ratio q_0/q_{av} to reach a specified value as a function of annealing temperature.

Figure 1 shows the time-temperature plots for 100 μm radius PuO_2 particles for $q_0/q_{av} = 2$. According to these curves, a sintered compact containing 5% plutonium in the form of 100 μm radius particles requires annealing at 2500°K for 350 hr. if the plutonium fraction at the original PuO_2 particle center is to be reduced to twice the average value. If the temperature is lowered to 2200°K, the required annealing time is 7600 hrs. To achieve the same degree of homogenization in less than 100 h would require temperatures in excess of 2600°K.

Fig. 1. Time-temperature plots for fuels originally containing discrete PuO_2 particles $100 \mu\text{m}$ radius to homogenize to the extent that the maximum plutonium concentration is twice the average value. The parameter q_{AV} denotes the ratio of Pu to total heavy metal content.

(XBL 7512-9235)

The required times and temperatures appear to be impractically large to render high temperature annealing a useful manufacturing method for homogenization of mixed oxide fuels fabricated from blended powders. The numerical results cited above, however, depend very strongly on the cation diffusion coefficient in the mixed oxide. In view of the substantial uncertainty in the U-Pu mutual diffusion coefficient, it appears worthwhile to experimentally verify the feasibility of high temperature homogenization of mixed oxide fuels on production-grade samples. To capitalize on the beneficial effect of large oxygen-to-metal ratios on the cation diffusion coefficient, the homogenization anneal should be performed prior to hydrogen reduction.

* Published in J. Nucl. Mater. 60, 237 (1976).

7. RESEARCH PLANS FOR CALENDAR YEAR 1977

Donald R. Olander

Theoretical studies of fuel homogenization will be extended to the in-reactor case. The effects of nonuniform temperature distribution and radiation-enhanced cation diffusion will be taken into account.

A molecular beam study of the cracking of silane to produce thin film silicon will be started. The object of the work is to elucidate the mechanism of the deposition reaction. This reaction is used for producing electronic components and photovoltaic devices for direct solar energy conversion.

The molecular beam experiment on the reduction of UO_2 by atomic hydrogen will be extended to investigate the effect of using hypostoichiometric and single crystal UO_2 specimens on the kinetics. Alumina reduction studies will be started.

The laser pulsing of UO_2 experiment will concentrate on mass spectrometric identification of the species emitted from the surface during the vaporization transient. The angular distribution of the vaporizing UO_2 will also be measured.

The solubility of hydrogen in UO_2 and Al_2O_3 will be investigated in a high temperature, high pressure furnace. This phenomenon is important in understanding the fabrication process for UO_2 fuel and in assessing the effectiveness of ceramic oxide coatings on CTR components for tritium containment.

The thermal gradient migration studies of small metallic particles in urania will continue. In addition to UO_2 , migration in Al_2O_3 will also be investigated using single crystal ruby specimens.

Work on oxygen self-diffusion in hypostoichiometric urania will continue. The method involves a diffusion couple consisting of UO_{2-x} and UO_{2-x} wafers bonded by a liquid uranium film and determination of the $\text{O}^{18}/\text{O}^{16}$ ratio by mass spectrometric analysis of the $\text{H}_2\text{O}^{18}/\text{H}_2\text{O}^{16}$ ratio in the water vapor produced by H-atom reaction with the back face of the couple.

Using the newly installed focusing magnet, the radiation chemistry of $\text{H}_2/\text{CO}_2/\text{He}$ and $\text{H}_2\text{O}/\text{CO}/\text{He}$ mixtures and the radiation-enhanced corrosion of graphite will be investigated. These phenomena are important in assessing the performance of coolant corrosion in high temperature gas-cooled reactors.

8. 1976 PUBLICATIONS AND REPORTS

Donald R. Olander and Associates

Book

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Journals

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Energy and Angle of Incidence, Surf. Sci. 54, 154 (1976).

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Papers Presented

1. D. R. Olander, Molecular Beam Studies of Atomic Hydrogen on Oxide Surfaces, Bay Area Conference on High Temperature Science and Technology, April 22, 1976, NASA Ames Research Center.

2. D. R. Olander, Chemical Erosion of Ceramics, CTR Electrical Insulator Meeting, Los Alamos Scientific Laboratory, May 17, 1976.

3. D. R. Olander, Surface Chemical Kinetics by Modulated Beam Mass Spectrometry, Inter. Conf. on Colloids and Surfaces, American Chemical Society, San Juan, Puerto Rico, June 21, 1976.

4. D. R. Olander, Molecular Beam-Mass Spectrometric Studies of the Reduction of UO_2 by Hydrogen, Centre d'Energie Atomique, Fontenay-aux Roses, France, August 31, 1976.

5. D. R. Olander, Molecular Beam Studies of High Temperature Gas-Solid Reactions, Surface Science and Catalysis Seminar, LBL, October 13, 1976.

6. D. F. Dooley, Reduction of Urania by Atomic Hydrogen, American Ceramic Society Meeting, November 1, 1976, San Francisco.

* Supported by the FOM Institute of Atomic and Molecular Physics, Amsterdam.

c. Process Technology of Solid-State Materials

Lee F. Donaghey, Principal Investigator

Introduction. This research program is concerned with the synthesis and processing of solid-state materials for energy conversion applications. Of particular interest are chemically reactive processes useful in the preparation of crystalline films and coatings, such as chemical vapor deposition, reactive sputtering and solution crystal growth.

The program utilizes the coordinated contributions of several subprograms: (1) reaction kinetics of growth and etching, (2) thermodynamic and phase equilibrium of inorganic compounds and solutions, (3) computer simulation and analysis of synthesis processes, (4) preparation of important solid-state materials, (5) characterization of electrical, optical, and structural properties and (6) process control. These subprograms are directed at deducing the influence of process variables on important structural and electronic defects, and at establishing a comprehensive basis for industrial process design.

1. REACTION KINETICS

a. Vaporization Kinetics of (100) GaP*

Carlos Figueroa and Lee F. Donaghey

The vaporization kinetics of (100) GaP was studied in the temperature range from 550 to 850°C using thermogravimetric analysis.

GaP samples were prepared by cutting oriented, thin sections from GaP single crystals. The sections were then mechanically polished to a 0.1 μm diamond finished, then etched with a polishing etchant. The samples were then thoroughly cleaned of organic and heavy metal contaminants before placement in the thermogravimetric apparatus. The surface orientation and morphology were examined by x-ray diffraction and by scanning electron microscopy before and after each experiment.

The experimental evaporation rates of (100) GaP can be expressed by the following relations:

$$r(\text{mg cm}^{-2}\text{sec}^{-1}) = \begin{cases} 3.59 \times 10^4 e^{-35,480/RT}, & T > 680^\circ\text{C} \\ 4.73 \times 10^{20} e^{-109,250/RT}, & T < 680^\circ\text{C}. \end{cases}$$

In these temperature ranges the etching reactions were confirmed to be

and

respectively.

GaP evaporation is postulated to occur by parallel reaction steps involving Ga(l) vaporization and P₂ desorption. The overall rate equation can be expressed as

$$r = (c_s(K_1\phi + K_2(1-\phi)))^{1/2}$$

where ϕ is the fractional coverage of the surface by liquid gallium. The model predicts an activation energy of 147.5 kcal/mole for the gallium vaporization reaction.

* Abstracted from LBL-5788

b. Vapor Phase Etching Kinetics of GaP in HCl-PH₃-H₂*

Carlos Figueroa and Lee F. Donaghey

The vapor phase etching of single crystal GaP in HCl-PH₃-H₂ was investigated in the temperature range from 550 to 850°C and for P_{total} < 1 Torr using thermogravimetric analysis.

Etching studies were carried out in a vertical, quartz-lined tube furnace, as the tube furnace is a basic container for high temperature gas-solid reactions in the semiconductor industry. A gas manifold was designed for maximum flexibility for fine metering of five gases. The microbalance used was a Perkins-Elmer AR-1 Autobalance, with a 5 g capacity.

The experimental HCl etching rate was observed to reach a maximum limit for a given partial pressure of HCl in the range T > 650°C and P_{HCl} > 0.1 Torr. The apparent activation energy for the etching reaction in the temperature range below 650°C was found to be 137 kcal/mole.

The GaP-HCl reaction mechanism is postulated to be a unimolecular surface reaction with dissociation of the HCl reactant. The overall rate equation for the GaP-HCl-H₂ reaction system can be expressed as follows:

$$r = K_2 \left(\frac{K_1 P_{\text{HCl}}}{P_{\text{H}_2} (1 + K_1 P_{\text{HCl}})} \right)^{1/2}$$

The kinetic model predicts activation energies for the following elementary steps:

P₂ desorption: 16 kcal/mole

H₂ dissociative adsorption: -56 kcal/mole

HCl adsorption: >80 kcal/mole

PH₃ adsorption: 60 kcal/mole.

Substituting the calculated results into the kinetic model, we obtain

$$r(\text{mg cm}^{-2}\text{sec}^{-1}) = 2.1 \times 10^{-3} \left(\frac{e^{16,000/RT}}{e^{56,000/RT} P_{\text{H}_2}} \right)^{1/2}$$

$$\times \left(\frac{K_1 P_{\text{HCl}}}{1 + K_1 P_{\text{HCl}}} \right)^{1/2}$$

where,

$$K_1 = e^{-274,000/RT} e^{288.8/R}$$

The rate limiting steps are suggested to be P_2 desorption for $T > 650^\circ\text{C}$ and HCl activated-adsorption for $T < 650^\circ\text{C}$.

* Abstracted from LBL-5788.

c. Effect of Mass Transfer on the High Temperature Etching Kinetics of GaAs

Lee F. Donaghey

Vapor-phase etching of GaAs is industrially important for *in situ* surface preparation prior to vapor phase growth by chemical vapor deposition.¹

The etching rate of GaAs at the high temperatures utilized in industrial, vapor phase growth processes can be expected to be strongly influenced by mass transfer processes. In several of the early studies of GaAs growth in open systems, growth rates were estimated from the thermodynamic yield. The stagnant-film model for diffusion-controlled growth has been employed in more recent studies of chemical vapor deposition, yet the actual conditions of fluid flow in the immediate region of the etching surface are expected to influence the species fluxes to the surface, and consequently, the etching rate. In this study, high temperature corrections needed to calculate the etching kinetics were studied for various hydrodynamic conditions, and the etching rates were compared to the rates calculated from the simplified film model. Correction factors for all models considered deviated significantly from unity with increasing temperature and with increasing atom fraction of chlorine in the etching gas.

1. S. A. Shaikh, H. K. Chou and L. F. Donaghey, Abstract 151, p. 364, Electrochemical Society Extended Abstracts, Spring Meeting, San Francisco, Calif., May 12-17, 1974.

2. THERMODYNAMICS

a. Gibbs Energy of Formation of β -Gallium Sesquioxide*

Timothy J. Anderson and Lee F. Donaghey

The Gibbs energy of formation of β -Ga₂O₃(c) was determined with a high-temperature, solid-state electrochemical cell utilizing calcia-stabilized zirconia as the solid electrolyte and a CO - CO₂ gaseous mixture as the reference electrode. The Nernst voltage of the cell,

was measured over the temperature range from 775 to 1100 K. A linear regression analysis of the data showed that the Gibbs energy of formation can be represented by

$$\Delta G_f^0(\text{Ga}_2\text{O}_3, \text{c}, T) / \text{kcal}_{\text{th}} \text{mol}^{-1} =$$

$$(-265.83 \pm 0.16) + (0.08345 \pm 0.00016)(T/\text{K})$$

A comparison of the results with those of other studies is shown in Fig. 1.

Fig. 1. Gibbs energy of formation of β -Ga₂O₃ as a function of temperature. (---○---) Experimental data from this study. (—) Coughlin, (.....) Pankratz and Kelley, (-·-·-) Smith and Chatterji, (-----) Klinedinst and Stevenson (coulometrically titrated oxygen), and (--- --) Klinedinst and Stevenson (Ga, β -Ga₂O₃ electrode). (XBL 757-6775B)

A third law analysis of the data showed that the standard enthalpy of formation is $-261.0 \pm 0.1 \text{ kcal}_{\text{th}} \text{mol}^{-1}$.

The results of the third-law analysis show a temperature dependence of $0.004 \text{ kcal}_{\text{th}} \text{ mol}^{-1} \text{ K}^{-1}$, which is most probably caused by an error in the estimated high temperature heat capacity of gallium rather than by electronic conduction in the solid electrolyte.

Indeed, it appears that no measurements of the specific heat of gallium have been made above 720 K, and the assumption of a constant specific heat in this temperature range is probably in error. Nevertheless, the direct measurement of $\Delta G_F^\circ(\beta - \text{Ga}_2\text{O}_3)$ performed in this study showed much better consistency with the calorimetric data than did the data from earlier emf studies, as shown by both second-law and third-law analyses.

* Abstracted from LBL-4128 Revised.

b. Gibbs Energy of Formation of Indium Sesquioxide*

Timothy J. Anderson and Lee F. Donaghey

The Gibbs energy of formation of In_2O_3 was studied in the solid-state electrochemical cell,

over the temperature range from 950 to 1128 K, using calcia-stabilized zirconia as the solid electrolyte and a $\text{CO} + \text{CO}_2$ gaseous mixture as the reference electrode. The Nernst equation was used to derive data on the Gibbs energy of formation of indium oxide. A linear least-square regression analysis of the data gave

$$\Delta G_F^\circ(\text{In}_2\text{O}_3, \text{c}) / \text{kcal}_{\text{th}} \text{ mol}^{-1} =$$

$$(-223.67 \pm .14) + (8.044 \pm 0.014) \times 10^{-2} (T/\text{K}) .$$

A third-law analysis of the data showed that

$$\Delta H_F^\circ(\text{In}_2\text{O}_3, \text{c } 298.15) / \text{kcal}_{\text{th}} \text{ mol}^{-1} = -222.09 \pm 0.01$$

in agreement with calorimetric determinations. However, the results of previous studies showed considerable deviations in the standard enthalpies and entropies of formation, as shown in Fig. 2. As indicated our results showed much better consistency with the calorimetric result of Holley, et al.¹ The values of the enthalpy of formation of Ga_2O_3 at 298.5 K calculated by the third law method also gave the most temperature independent values and were in close agreement with calorimetric data.

The microcomputer automation of the study proved exceptionally beneficial for automatic testing of thermodynamic equilibrium and of the reproducibility of the data. The results of the study gave the most temperature-independent values of $\Delta H_F^\circ(\text{In}_2\text{O}_3, \text{c}, 298.15)$ of all the emf studies of the $\text{In}_2\text{O}_3(\text{c})$ formation reaction, and

Fig. 2. Standard enthalpy of formation of $\text{In}_2\text{O}_3(\text{c})$ obtained by a third-law analysis of the experimental data: (•) This work; (x) Schaefer; (Δ) Klinedinst and Stevenson; (---) Chatterji and Vest; (— · —) Newns and Pelmore; (— · —) Bird et al.; (—) Holley, Huber and Neierkord; (— · —) Becker and Roth. (XBL 758-6785A)

in close agreement with calorimetric data. No evidence was found for the formation of $\text{In}_2\text{O}(\text{c})$ over an $\text{In}(\ell) + \text{In}_2\text{O}_3(\text{c})$ coexistence electrodes.

* Abstracted from LBL-4137 Revised.

1. C. E. Holley, E. J. Huber, Jr., E. H. Neierkord, J. Am. Ceram. Soc. 74, 1084 (1952).

c. Component Activities in Ga-Sb Liquid Alloys*

Timothy J. Anderson and Lee F. Donaghey

Component activities in Ga-Sb liquid alloys were studied in the high temperature galvanic cells,

and

The cell of type 1 has the advantage of simpler operation while cell 2 does not require an independent determination of the Gibbs energy of formation of $\beta - \text{Ga}_2\text{O}_3$.

A survey of the available literature indicated the thermodynamic properties of the Ga-Sb binary liquid system are not well-established. Activities of Ga were investigated for both types of cells. The results are presented in Fig. 3 which shows component activities as a function of composition. Also shown are the results of

Fig. 3. Activities of gallium and antimony in the liquid mixture at 1003 K. —○—, this work; —, Yazawa, Kawaoshima and Itagaki; ---, Danilin and Yassenko; ·····, Gerasimenko, Kirichenko, Lozhkin, and Morachevskii. (XBL 757-6788)

previous work. Partial molar quantities were calculated from the observed temperature dependence and were found to be in general agreement with calorimetrically determined values.

In order to assess the accuracy of the results, liquidus temperatures for the Ga-Sb binary phase diagram were calculated in combination with the available calorimetric data. These results were found to be in excellent agreement with the experimentally determined phase diagram. A pair potential analysis was applied to these results to examine short range ordering in the liquid melts.

* Abstracted from LBL-4153

d. Thermodynamic Studies of Gallium-Indium Liquid Alloys by Solid State Electrochemistry with Oxide Electrolytes*

Raymond Pong and Lee F. Donaghey

Solid-state electrochemical methods are applicable to the study of the thermodynamic properties of Ga-In-group V semiconductor systems. The experimental investigations on the ternary requires that the available data on the corresponding binary systems be verified.

The activity of gallium in Ga-In liquid alloys was studied in a high-temperature galvanic cell using calcia stabilized zirconia as an oxide electrolyte. The measured activity data for gallium in the Ga-In melts was used to calculate the interaction coefficient in the liquid alloy,

which has the form $\alpha_{\text{GaIn}} = \ln \gamma_{\text{Ga}} / (1 - x_{\text{Ga}})^2 = 0.2862 + 0.0352x_{\text{Ga}} + (398.3 + 220.0x_{\text{Ga}})T^{-1}$. The derived expressions for the enthalpy and excess entropy of mixing were found to be given by $\Delta H^M = (791.4 + 218.6x_{\text{Ga}})x_{\text{Ga}}(1 - x_{\text{Ga}})$ and $\Delta S^{\text{xs}} = -(0.568 - 0.0350x_{\text{Ga}})x_{\text{Ga}}(1 - x_{\text{Ga}})$. The enthalpy of mixing reaches a maximum of 226 cal/mol at a gallium mole fraction of 0.53.

* Abstracted from LBL-4107

3. PROCESS ANALYSIS AND SIMULATION

a. Analysis of Transport Processes in Vertical Cylinder Epitaxy Reactors*

C. W. Manke and L. F. Donaghey

Momentum, heat, and mass transfer processes were studied for the epitaxial growth of Si from SiCl_4 in H_2 by chemical vapor deposition in a vertical cylinder reactor. An analytical solution to the problem of heat and mass transfer in a tapered annulus were developed based on constant transport properties and fully-developed laminar flow. The mean gas-phase temperature and deposition rate distribution of silicon calculated within the reactor using the developing temperature model. Results of experiments, and of other experimental studies of silicon deposition from SiCl_4 in H_2 at 1200°C in a vertical cylinder reactor were compared with the analytical results, and with other models of diffusion-controlled chemical vapor deposition. The developing temperature model is shown to be highly accurate for predicting deposition rates for Reynolds numbers between 10 and 50. This study provides an analytical basis for predicting epitaxial deposition rate distributions in vertical cylinder reactors, and for reactor design to improve the yield and uniformity of epitaxial growth.

* Abstracted from LBL-5187

b. Numerical Simulation of Transport Processes in Vertical Cylinder Epitaxy Reactors

Charles W. Manke and Lee F. Donaghey

The modeling of epitaxial silicon growth by chemical vapor deposition has received considerable attention in the literature, both for reactor design purposes and for understanding experimental phenomena. In a previous study, the authors show that reactant gas temperature development occurs over a large portion of the susceptor and exerts a strong influence on growth rate distribution over the front part of the susceptor. A method was developed for calculating the growth rate distribution along the vertical reactor susceptor that accounted for the effect of developing gas temperature profile, but with average transport properties

assigned to the reactant mixture. In this study, a numerical method employing a marching iteration of finite difference equations is used to solve for the momentum, temperature, and component mass concentration profiles in the tapered annulus of a vertical cylinder epitaxy reactor.

Results of the study show that the numerical solution of the parabolic equations chosen to model momentum, heat, and mass transfer in the barrel reactor gives a much closer approximation to the coupled solution of these equations in developing flow than the Developing Temperature Model. The numerical results have been used to test the accuracy of the Developing Temperature Model under different flow conditions. The Developing Temperature Model and the numerical solution are in reasonable agreement at Reynolds numbers up to about 100, as shown by Fig. 1.

Fig. 1. Variation of growth rate with position along the susceptor, comparing results of the numerical computation (—) and the developing temperature model (-----). (XBL 773-5196)

Growth rates calculated by the numerical method are higher at the entrance of the reactor than rates predicted by the Developing Temperature Model, but further downstream the numerical curves drop below the curves calculated from the Developing Temperature Model. The more rapid decline of the growth rates predicted by the numerical method results from reactant depletion. Since deposition is higher in the leading edge region, the reactant is depleted more rapidly and downstream growth rates are lower. The growth rate distributions predicted by the Developing Temperature Model and the numerical solution are quite different at Reynolds numbers greater than 100, where the assumptions used to derive the Developing Temperature Model break down.

c. Investigation of Buoyancy Effects on Transport Processes in Chemical Vapor Deposition Reactors

Charles W. Manke and Lee F. Donaghey

Buoyancy effects in vertical-cylinder epitaxial growth reactors are under study to determine the effects of buoyancy on momentum, heat and mass transport processes, toward the development of design considerations optimizing the performance of reactors for epitaxial growth. While the

problem of mixed convection over a vertical semi-infinite flat plate has been studied by a number of investigators,^{1,2} the problem of mixed convection in confined flows has apparently received little attention. Buoyancy effects have considerable relevance to CVD processes, however, particularly in cold-wall reactors where the reactant flow is confined by a channel formed by a hot, vertical susceptor and a parallel, air cooled outer wall.³

For the case of confined flow, the problem of flow downward between parallel plates was studied. The velocity profiles were determined in the zone of the reactor where the temperature distribution was fully established in the channel. Calculated velocity profiles were determined for fixed values of the Grashof-Reynolds number ratio, relative to the critical ratio for the onset of reverse flow.

From the analysis of velocity distribution in mixed convection between parallel plates, the critical value of Gr/Re at which flow reversal occurs at the inner wall was determined to be 18. The typical range of Gr/Re ratios for epitaxial deposition of silicon³ is from 4 to 8. This result indicates that the velocity profiles in such chemical vapor deposition (CVD) processes are stable against flow reversal. The velocity gradient at the wall is significantly different from that calculated for the isothermal reactor, and this effect changes the chemical vapor deposition rates.

The present study is being extended to obtain solutions to the modified Graetz problem for mass transfer in vertical channels.

1. A. Acrivos, Chem. Eng. Sci. 21, 343 (1966).
2. E. M. Sparrow et al., Phys. Fluids 2, 319 (1959).
3. C. W. Manke, (M.S. thesis) LBL-5187, University of California, Berkeley (1976).

4. CHEMICAL VAPOR DEPOSITION

a. Chemical Vapor Deposition of GaAs by Pyrolysis of $Ga(CH_3)_3$ and AsH_3

Alice L. Lin* and Lee F. Donaghey

Vapor phase deposition of gallium arsenide from trimethyl gallium (TMG) and arsine offers several advantages as compared to the conventional growth technique using halogen compounds. This method is free of etching effects and from contamination by chemical transport of elements from the container, requires a furnace with only one temperature zone, and offers the possibility of lower growth temperature. Recently, single-crystal GaAs films were successfully prepared by this method in several industrial laboratories. Yet little information on growth kinetics has been reported for GaAs growth on C or Mo substrates. The purpose of the present study was to examine in detail the effects of growth conditions on the deposition rate and morphology of homoepitaxial GaAs layers.

The growth apparatus consisted of a water-cooled vertical quartz reactor containing a pyrolytic graphite pedestal which supported substrate crystals. Trimethyl gallium was contained in a saturator through which hydrogen gas was sparged. The deposition rate of GaAs vs. AsH₃ mole fraction was found to be independent of AsH₃ concentration as long as the input mixture contained a three-fold excess of AsH₃ over TMG. The growth rate varied linearly with the TMG concentration.

The dependence of the deposition rate on temperature and reactant flow rate is consistent with a diffusion controlled model over the temperature range from 700 to 900°C. Thermochemical studies show that the TMG partial pressure on the surface of deposition is negligible. A

mass transfer model based on the hydrodynamics of an impinging gas jet predicts diffusion controlled growth rates a factor of 3 higher than the experimental rates. These results suggest a complex kinetic reaction limitation for the deposition process.

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b. Evaluation of Substrate Materials for Low Cost GaAs Solar Cells

Rémy de Barnardy, Alice L. Lin and Lee F. Donaghey

Low cost substrate materials were evaluated for application in solar cells utilizing GaAs

Fig. 1. Scanning electron micrographs of GaAs films deposited on different materials: (a) stainless steel, (b) tantalum, (c) molybdenum, (d) tungsten, (e) pyrex and (f) graphite. Growth conditions were:

temperature: 750°C;
hydrogen flow rate: 1 l/min.;
Ga/H = 0.082;
As/Ga = 29;
Growth time: 10 min.

(XBB 7611-10437)

deposited by chemical vapor deposition from trimethylgallium and arsine in a hydrogen carrier gas. The microstructural and electrical properties of the films were studied to determine the effects of the different substrate materials on film and interfacial properties. Of particular interest were the grain size and growth morphology of GaAs crystallites, the interfacial reaction products formed between and GaAs and the metal during growth, and the resulting electrical contact resistance between the film and metal.

Ideally, the substrate used for low-cost solar cells should be available in thin sheets at low or moderate cost and should not react with gaseous reactants or with GaAs under the conditions of the deposition. Also, the thermal expansion coefficient should match sufficiently with that of GaAs so as to avoid plastic deformation of the film during cooling from the film deposition temperature. The film obtained should have a strong adherence with the substrate and exhibit large grain size with columnar structure. Electrical properties of interest are high conductivity of the substrate and low ohmic contact resistance to GaAs, so that the metal can be utilized as one of the electric contacts of the cell.

The morphology of GaAs films deposited on several metals potentially useful as substrates for GaAs solar cells are shown in Fig. 1. Of the metals considered, nickel and iron-base alloys offer the lowest cost, but with the largest mismatch in the coefficient of thermal expansion.

Tantalum matches the coefficient of thermal expansion of GaAs most closely, but has one of the highest costs of substrate metals. Molybdenum is available at a relatively low cost, but has a coefficient of thermal expansion which differs from that of GaAs by 14%. The grain size on all substrates was distributed, indicating continuous nucleation during the growth process.

Of the substrate materials studied, Mo, glass and graphite, graphite appears to give the largest grain size in GaAs films without forming interfacial reaction products. Thus, graphite and Mo appear to have adequate physical and electrical properties for solar cell applications.

c. Chemical Vapor Deposition and Properties of GaAs on Molybdenum Substrates*

Rémy C. de Barnardy[†] and Lee F. Donaghey

GaAs is one of the most promising semiconducting compounds for the preparation of terrestrial solar cells: its favorable band gap energy in relation to the solar-energy spectrum results in the highest predicted photovoltaic conversion efficiency, its high absorption coefficient is such that a layer of a few microns in thickness is sufficient to absorb almost all of the incident sunlight, implying a low consumption of material in solar cells. Also, this compound can be used at a significantly higher temperature than its competitors without an important loss of conversion efficiency.

Fig. 2. Scanning electron micrograph of GaAs layers deposited on molybdenum at different substrate temperatures. The growth time was 15 min, As/Ga = 24, and S/H = 3.2×10^{-5} .

(a) 600°C, (b) 700°C, (c) 875°C, (d) 950°C.

(XBB 769-8370)

The chemical vapor deposition of GaAs on metallurgical grade molybdenum, using trimethylgallium and arsine in hydrogen, was studied toward the realization of cost effective solar cells for terrestrial applications. The influences of substrate temperature, reactant mole fractions and H_2S dopant on the microstructural properties of the deposited layers were studied. X-ray diffraction analysis showed that the GaAs films were randomly oriented with a (220) preferred orientation parallel to the substrate.

The grain size of GaAs crystallites in the range from 1 to 4 μm increased with increasing substrate temperature, up to 950°C, where molybdenum and arsenic formed reaction products of the substrate. A comparison of the surfaces of approximately 5 μm thick films deposited at different substrate temperatures from 600 to 950°C is shown in Fig. 2. The figure shows that the grain diameter increases with substrate temperature from less than 1 μm at 600°C to up to 5 μm at 875°C.

A practical temperature range which appears suitable for preparation of films for solar cells is 700°C < T < 875°C.

The introduction of a H_2S dopant with mole fraction below 2×10^{-4} was found to have no significant influence on the morphology of GaAs films.

* Abstracted from LBL-5736

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d. Preparation and Properties of Chemically Vapor Deposited GaAs on Graphite*

Rémy C. de Bernardy and Lee F. Donaghey

Toward the realization of cost-effective GaAs solar cells for terrestrial application, polycrystalline GaAs films have been deposited on graphite by chemical vapor deposition using trimethylgallium and arsine in a hydrogen carrier gas.

Fig. 3. Effect of substrate temperature on the growth rate of GaAs on unpolished graphite. (XBL 769-7546)

Fig. 4. Comparison of substrates and GaAs films deposited on (first row) unpolished, (second row) mechanically polished, and (third row) sandblasted graphite. First column: SEM micrograph of substrate surfaces before deposition, Second and third rows: GaAs films, at different magnifications. Fourth row: vertical cross sections of deposited GaAs layers. Growth conditions: substrate temperature, 750°C; H_2 flow rate 7.44×10^{-4} mole/s (1 l/min); TMG mole fraction, 0.041%; As/Ga molar ratio, 30; deposition time; 40 min. (XBL 769-8659)

GaAs films with thicknesses between 5 and 50 μm were deposited under different conditions of growth. The films were all found to be polycrystalline with grain size decreasing with increasing film thickness.

Higher concentrations of TMG were found to produce higher growth rates, as expected. Surprisingly, larger crystallites were obtained at higher growth rates, up to a maximum size of about 5 μm at TMG molar concentrations greater than 0.6×10^{-3} . Measured growth rates were found to be larger on graphite than on (100) GaAs, and to depend also on the defect density of the substrate.

The mechanisms for growth in different temperature ranges are summarized in Fig. 3. At temperatures below 680°C, and above 960°C, dendritic growth predominates. Surface reaction controlled growth appears to prevail between 680°C and 750°C, while diffusion controlled growth dominates between 750°C and 960°C. The diffusion controlled growth regime spans a wider temperature range than the corresponding growth on (100) GaAs, shown by the dotted line in Fig. 3 as reported by Lin and Donaghey.¹

Grain size up to 5 μm could be achieved with high substrate temperatures below 960°C and trimethylgallium mole fractions near 10^{-3} . A comparison of graphite surfaces before and after deposition, with unpolished, mechanically polished and sand blasted graphite substrates is shown in Fig. 4, for growth at 750°C. Surface preparation of metallurgical graphite by mechanical polishing was shown to reduce the surface defect density, but introduced holes in deposited films. Sandblasting of the graphite substrates produced increased roughness in the deposited films.

Attempts were made to prepare Schottky barrier solar cells using 5 μm thick layers of GaAs grown at 750°C. The cells prepared exhibited a low short circuit current and very high series resistance, possibly because of the high resistance of the graphite/GaAs interface.

* Abstracted from LBL-5737

1. A. Lin and L. F. Donaghey, Chemical Vapor Deposition of GaAs by Pyrolysis of $\text{Ga}(\text{CH}_3)_3$ and AsH_3 , LBL-5734, November 1976.

e. Preparation of Schottky-barrier Solar Cells from Polycrystalline GaAs on Molybdenum*

Rémy C. de Bernardy and Lee F. Donaghey

Polycrystalline GaAs Schottky-barrier solar cells have been prepared by chemical vapor deposition of a 4 μm thick layer of n-type GaAs onto metallurgical-grade molybdenum, and by sputter deposition of gold surface electrodes. Prior to GaAs deposition, the metal was chemically polished in a 6:2:1 mixture of nitric:lactic:hydrofluoric acid, then degreased. GaAs was

deposited at 0.4 $\mu\text{m}/\text{min}$ at 750°C. Samples grown were intentionally doped with sulfur to a carrier concentration of about 10^{17} cm^{-3} .

The open-circuit voltage of the device is 0.34 V. The short-circuit current density of 3.7 mA/cm^2 is low because of a high series resistance. The equivalent AMI efficiency is 1.3% with an anti-reflection coating. The current-voltage response of the cell under a 100 mW/cm^2 of water filter tungsten illumination is shown in Fig. 5.

Fig. 5. V-I characteristics of the Au/n-GaAs/Mo solar cell under water-filtered 100 mW/cm^2 tungsten illumination. (XBL 7610-7671)

The low open-circuit voltage corresponds to a shunt resistance of 100 Ω/cm^2 , and to a series resistance of 70 Ω/cm^2 . Both series resistance and shunt conductance should be reducible by improvements in processing and in cell design.

* Abstracted from LBL-5727.

5. REACTIVE SPUTTERING

a. Effect of Target Oxidation on Reactive Sputtering Rates of Titanium on Argon-Oxygen Plasmas*

Lee F. Donaghey and Kenneth G. Geraghty[†]

Reactive sputtering is an important industrial process used for the preparation of dielectric films for optical and electronic applications. The reactive sputtering process involves the sputtering of a target material in a plasma

containing a partial pressure of a reactive gas such as oxygen. An important problem with this process is that the sputtering target can be oxidized by the reactive gas. As a consequence of target oxidation, significant transients can occur in reactive sputter rate processes and also in the stoichiometry of the deposited compound film. It is important to establish the criteria for the onset of target oxidation and its effect on rate processes for the optimal design of industrial reactive sputtering processes. In this study, the factors determining the onset of target oxidation of titanium are explored during rf sputtering in an argon-oxygen plasma.

Reactive sputtering rates of titanium in argon-oxygen plasmas were studied as a function of oxygen and argon partial pressures in an rf diode sputtering system at 2 keV bias voltage. The sputtering rate changed by an order of magnitude at a critical oxygen mole fraction in the plasma equal to 0.0070.

A material balance on oxygen incorporation and etching was developed to show that the target sputtering yield, S_{Ar} , oxidation probability α_{O_2} and target oxygen mole fraction x_0 are related by

$$\frac{x_0 S_{Ar}}{\alpha_{O_2}} \approx \frac{y_{O_2}}{1 + \beta y_{O_2}}$$

where y_{O_2} is the mole fraction of O_2 in the plasma, and β is a constant with unity magnitude. Threshold for target oxidation is essentially independent of the total plasma pressure, and specified uniquely by a critical mole fraction of oxidant in the plasma.

* Abstracted from LBL-4110

† Present address: General Dynamics, Pomona, Calif.

b. Preparation of Suboxides in the Ti-O System by Reactive Sputtering*

Kenneth G. Geraghty[†] and Lee F. Donaghey

The preparation of nonstoichiometric TiO_x films by reactive sputtering of titanium in an argon-oxygen plasma was studied in a rf diode sputtering system at 2 keV bias voltage. The properties of titanium oxide films deposited from oxidized and nonoxidized Ti targets were explored to determine the composition of the deposited phases. The mole fraction of oxygen, x , in the deposited films was determined from a combined analysis of film density, and UV and IR spectra. The stoichiometry of the target surface and of the deposited films is shown in Fig. 1 as a function of oxygen mole fraction in the plasma. The results indicate that phases with $x=0$, 1.0, and >1.6 (the Magneli phases and TiO_2), can be readily produced during reactive sputtering in argon plasmas containing an oxygen mole fraction in the range from 0 to 0.15. The deposition of suboxide phases other

Fig. 1. Oxygen mole fractions in the sputter deposited TiO_x films and on the surface of the titanium target, as a function of the oxygen mole fraction in the plasma, y . (XBL 7612-10980)

than αTiO_8 , $TiO_{1+\delta}$ and $TiO_{2-\delta}$ required stringent control of the processing variables not easily produced. This result would indicate that reactive sputtering can be effectively utilized to produce certain species of titanium oxides, provided the sputtering parameters are controlled.

* Abstracted from LBL-4980

† Present address: General Dynamics, Pomona, Calif.

c. Study of Factors Affecting Rate Transitions of Reactively Sputtered Titanium Nitrides*

Roger F. Gentile and Lee F. Donaghey

Rate transitions are known to occur in the reactive sputtering rate of a metal with

Fig. 2. Deposition rate of TiN_x films as a function of reactive gas composition (system pressure: 10 mTorr; power density: 2.4 W/cm^2 ; target bias: 1.9 kV). (XBL 7611-7840)

increasing reactive gas content of the plasma. These transitions are expected to correspond to different oxidation states of the target. In this study, transitions in the sputter deposition rate of TiN_x formed by the reactive sputtering of Ti in an Ar - N_2 plasma are explored as a function of sputtering parameters.

The effect of substrate bias on the critical nitrogen mole fraction in the plasma leading to the principal rate transition is shown in Fig. 2. These results show that the small negative bias causes a decrease in the nitrogen adsorbed on the film, and shifts the threshold nitrogen concentration y^* to lower values.

Fig. 3. Chemical composition of TiN_x deposited films as a function of reactive gas composition (system pressure: 10 mTorr; power density: 2.4 W/cm^2 ; target bias: 1.9 kV).

(XBL 7611-7843)

Figure 3 shows the chemical composition of the deposited films. The transition corresponds to the onset for the deposition of TiN. Furthermore, the amount of nitrogen incorporated in the film for $y < y^*$ show that this transition correspond to the saturation of the deposited Ti film with nitrogen.

* Abstracted from LBL-5789

d. Study of Compound Formation of the Sputtering Target During the Reactive Sputtering of Ti with N_2 , C_2H_2 , and CH_4 *

Roger F. Gentile and Lee F. Donaghey

For the reactive sputtering of α -Ti in an Ar- N_2 plasma, titanium nitride was shown to form on the target in a cone morphology with a partial

coverage of the surface at a critical, low concentration y^* of nitrogen in the plasma. In addition, a thin layer ($<100 \text{ \AA}$) of amorphous TiN appears to form on the surface, with thickness increasing with the nitrogen concentration in the plasma.

Similar studies were performed with methane and acetylene as reactive gases, under conditions required for the deposition of TiC. Plasma polymerization occurred at large concentrations ($>5\%$ in Ar).

In all studies, the layer formed on the target were amorphous. Quantitative calculations of the deposition rates from Ti, TiN and TiC targets were compared to theoretical calculations based on Sigmund's theory¹ modified for a compounded target.² The results were in good agreement with the fact that the target surface is pure Ti for $y < y^*$ while it is TiN or TiC for $y > y^*$.

* Abstracted from LBL- 5789.

1. P. Sigmund, Phys. Rev. 184, 12, 383 (1963).
2. A. Nghi and R. Kelly, Can. J. Phys. 48, 137 (1970).

e. Reactive Sputter Deposition and Properties of Titanium Carbonitrides Thin Films*

Roger F. Gentile and Lee F. Donaghey

The nitrides, carbides, and carbonitrides of titanium are very hard compounds with potential application as wear, erosion and corrosion resistant coatings. Reactive sputtering is a potential method for depositing them, since this method provides excellent film adhesion, and allows control on the coating structure and chemical composition.

In this study the sputtering requirements and properties of TiN_x , TiC_x , and TiN_xC_y films formed by reactive sputtering of Ti in argon plasmas containing nitrogen, methane and acetylene were explored. The properties studied included the chemical compositions, film density, electrical resistivity, and adhesion to glass and titanium substrates. At a critical concentrations of reactive gases in the plasma, y^* , a step decrease in the sputter deposition rate occurred. For plasma compositions near y^* , the deposited film showed unusual properties or a sudden change in their properties.

For a large range of nitrogen composition in the plasma, the deposited film composition was TiN_x ($0.9 < x < 1.1$). The film density and resistivities were higher than the values of bulk TiN, but all other properties were fairly constant. This led to the conclusion that the rate limiting step for the compound formation is the sputtering of Ti from the target.

For the deposition of TiC_x and TiN_xC_y films, plasma polymerization of the hydrocarbons occurred. Therefore, compositions close to TiC or TiC_xN_y

were obtained only at very low reactive gas compositions.

* Abstracted from LBL-5789.

6. CHARACTERIZATION

a. Characterization of (111) GaAs and (111) InP Substrate and Homoepitaxial Layers by Divergent X-ray Beam Diffraction*

Alice L. Lin and Lee F. Donaghey

GaAs and InP substrates are the most commonly used III-V compound substrates for devices made by epitaxial growth. Heteroepitaxial layers are grown on (111) surfaces, for some optoelectronic applications. Because lattice imperfections play an important role in epitaxial growth, it is desirable to characterize these features by a fast and nondestructive technique. In this study the back-reflection divergent x-ray beam diffraction technique has been applied to the characterization of (111) GaAs and (111) InP substrates and homoepitaxial layers with different states of surface perfection. Diffraction conditions for generating back-reflection pseudo-Kossel patterns from (111) GaAs and (111) InP are presented.

The LPE growth of GaAs on GaAs (111)B substrates was carried out by a horizontal sliding-graphite boat system where an as-saturated Ga melt was placed above the substrate. A constant cooling rate of 2.3 °C/min was used during the growth process.

Mechanical polishing was observed to produce x-ray diffraction line broadening. Uneven line broadening was found to be produced by an inhomogeneous distribution of dislocations.

The chemically polished InP (111)B surface was found to give residual lattice strains which were comparable to those measured for the chemically polished InP (111)A surface.

The diffraction angles for pseudo-Kossel lines were influenced by subgrain tilting in epitaxial, LPE-grown layers. A close relationship between diffraction line profiles and surface morphology of the epitaxial layer was demonstrated with interference-contrast optical microscopy.

* Abstracted from LBL-5494

b. Erosion Properties of Reactively Sputter-Deposited Titanium Carbonitride Films

Roger F. Gentile and Lee F. Donaghey

The compounds TiN, TiC, TiC_xN_y are potentially useful as erosion resistant coatings.¹ The erosion properties of such compounds coating deposited by reactive sputtering have been studied

as a function of deposition conditions. The reactive gases used were N₂, CH₄ and C₂H₂ mixed with argon. Erosion test results were compared to the microhardness of the coatings, and to erosion mechanisms examined by scanning electron microscopy.

The TiN_x deposited films were found to have erosion resistant properties which were independent of the reactive plasma composition. A substrate bias increased the grain size and erosion resistance of such films.

Using CH₄ and C₂H₂ as reactive gases, both TiC_y and TiN_xC_y films were carbon rich since plasma polymerization occurred. The most erosion resistant films were those with composition close to TiC.

The erosion rates were enhanced by high erosion at grain boundaries leading to the removal of subgrains from the film. Annealing of the films following sputter deposition decreased the erosion resistance due to the formation of grooves at grain boundaries.

The mechanism of nucleation and growth of the film is dependent upon the substrate employed.² Films deposited on glass were much less adherent to the substrates and less erosion resistant. Their surface structure was also totally different.

This study showed the importance of the deposition conditions on the structure of a reactively sputtered coatings, and of the importance of substrate-plasma interactions on the film formation mechanism. The erosion properties of the coatings are closely related to these conditions and phenomenon.

1. G. Mah, C. W. Nordin and J. F. Fuller, J. Vac. Sci. Technol. **11**, 1, 371 (1976).
2. B. Laville St Martin, Thin Solid Films **4**, 319 (1969); **5**, 169 (1970); **6**, 359 (1970).

c. Engineering Evaluation of Solid Transition-Metal Sulfide Electrodes for Use in High Energy-Density Batteries*

Benjamin A. Marmaduke and Lee F. Donaghey

Solid electrode materials exhibiting anomalously high alkali ion diffusivities through layered structures were studied for application on high energy-density, fast discharge-rate batteries. The maximum storage capacity and maximum discharge rates were studied theoretically for a spectrum of transition metal sulfides which crystallize in the CdI₂ and MoS₂ structures. Simple criteria were established for screening potentially important solid electrode materials for battery applications.

The theoretical maximum storage capacity of various transition metal sulfides was determined for elements of the alkali metal series.

The activation energy for diffusion of the alkali ion between adjacent sites was determined

by summing the attractive, repulsive and polarization energies. The results of the calculation are shown in Table 1 for lithium.

Table 1. Chemical diffusivities of lithium in metal disulfides relative to $\text{Na}_{0.4}\text{TiS}_2$.

Metal Alkali Ion	Ti	Zr	Hf	Nb	Ta	Mo	W
Li, $x \rightarrow 0$	0.564	0.739	0.874	0.482	0.477	0.310	0.312
Li, $x \rightarrow 1$	0.491	0.672	0.618	0.410	0.403	0.278	0.312

The discharge rate was then deduced from a one-dimensional diffusion model with mobile ions diffusing from a planar electrode of finite thickness. The results showed that TiS_2 containing Na should have a higher discharge rate than all other electrodes examined.

The alkali ion discharge range is limited by shape stability requirements and by electrode voltage variation with mole fraction.

* Abstracted from LBL-5186.

d. Optimization of a Metal-Porcelain System for Applications in Prosthetic Dentistry*

Lee F. Donaghey

The design of an optimum metal-porcelain system for porcelain-fused crown-and-bridge dental applications is examined with emphasis on materials and process requirements and porcelain-fusing properties of new dental materials. Nickel-chrome alloys and matched aluminosilicate porcelains are shown to exhibit physical and thermochemical properties superior to precious metal alloys for porcelain-fusing applications. The bonding characteristics and the enhancement of the porcelain-metal bond strength by selective oxidation of alloying elements are studied experimentally with several commercial porcelains. The results of the study show that an optimum system can be achieved through the matching of thermochemical and physical properties of the metal alloy and the porcelain.

* Abstracted from LBL-5140.

7. PROCESS CONTROL

a. Microcomputer Systems for Chemical Process Control*

Lee F. Donaghey

Microprocessor-based microcomputers have significant potential for dedicated chemical process-control applications.

The microcomputer has introduced a unique compactness and modular simplicity to the process control field, and made possible a wide range of new applications that previously required a significantly more expensive dedicated computer.

In this paper, the results of the author's current program on microprocessor systems studies are presented to demonstrate and explore the range of feasible microcomputer applications to chemical process control. A primary objective of the author's current program has been to explore applications in technologically important chemical industries, but a secondary objective has been to develop general-purpose control systems for use in university-based chemical engineering research. The microcomputer systems described are based on the Intel 8008 and 8080 microprocessors, but interfaces and applications should be compatible and easily extended for use with other microprocessors.

The microcomputer systems currently used by the author in process-control studies make use of the bus-oriented modular-design approach developed at the Lawrence Livermore Laboratory.

The basic microcomputer system based on the Intel 8080 microprocessor has been developed on two card modules. Also, special-purpose interfaces have been designed on single cards.

The modular approach to microcomputer system design has facilitated the development of special-purpose microcomputer systems for application in chemical process control and in research. Table 1 summarizes the special features of several microcomputer systems developed in the author's laboratory. All of the specialty modules are functionally compatible with bin chassis for the Intel 8008 and 8080 microprocessor module sets, with few modifications, such as in backplane wiring of the bin chassis.

* Abstracted from LBL-4129.

b. A Microcomputer System for Real-Time Monitoring and Control of Gas Chromatographs*

L. F. Donaghey, G. M. Bobba,[†] and D. Jacobs[‡]

Microcomputer systems, based on the Intel 8008 and 8080 microprocessor, have been developed to perform real-time, on-line data acquisition and analysis of gas chromatographic data and to control sampling and operation of the gas chromatograph. Real-time analysis is achieved by the novel method of interleaving subprograms for the sequential data acquisition and reduction steps, thereby minimizing memory requirements. The system contains a real-time clock for signal timing, and interfaces to a teletype and digital voltmeter. An automated triac controller is used to control the temperature of the gas chromatographic column, while a matrix of relays is able to actuate sampling valves.

Table 1. Summary of special features of microcomputer systems developed in the author's laboratory.

System Features				
	Process Monitor	Gas Chromatography Analyzer	Electrochemical Experimental Controller	General-Purpose Digital Controller
System				
Hardware:	Tape Deck Control Circuit	Digital Voltmeter Interface	Digital Panel Meter Interface	Digital Panel Meter Interface
	Serial Teletype Interface	Serial Teletype Interface	Serial Teletype Interface	A/D Converter D/A Converter
	Digital Voltmeter Interface	Program Stack	Crystal-controlled Clock Circuit	Real-time Clock Reed Switch Matrix
		Real-time Clock	Control Latch	Control Latch
			Temperature Controller Interface	Solid-State Relays
			Input Multiplexer	High-Speed Reader
Memory:	1K×8 PROM	3K×8 PROM	2K×8 PROM	2 1/2K×8 PROM
	2K×8 RAM	1K×8 RAM	1K×8 RAM	3K×8 RAM
Software:	Input-Output Oriented Operating System	Research-Utility Operating System	Input-Output Oriented Operating System	Research-Utility Operating System
	Tape Drive Control	Floating-Point Math Package	DPM Read Routine	Floating-Point Math Package
	Process Monitor Program	Mean of N Points Standard Deviation	Equilibrium Test Routine	DPM Read Routine PID Control
	DVM Read Routine	Integration; Base Line Correction	Temperature Correction-Reset Routine	Sequencial Function Control

The operating speeds of the Intel 8008- and 8080-based microcomputer systems are compared. It is shown that the 8008-based system is compatible with digital voltmeters having sampling speeds exceeding 20 s^{-1} in chromatogram integration applications. The 8080-based system requires a high-speed A/D converter to prevent sampling rate limitations, and is capable of operating chromatogram integration and column heater control programs simultaneously.

* Abstracted from LBL-4138.

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c. A Microcomputer System for Analysis and Control of Multiple Gas Chromatographs*

G. Mario Bobba and Lee F. Donaghey

Gas chromatography is one of the most widely used techniques for quantitative analysis in the chemical industries and laboratories. Recent progress in computer automation has provided the means to solve the problem of automated gas chromatography.

The authors have recently developed and tested a microcomputer system for gas chromatography with automatic real-time sampling, data reduction, and control features.¹ This article describes an extension of the single gas chromatography controller with substantial improvement of that system so as to make possible the simultaneous control and real-time analysis of many gas chromatographs. The new microcomputer system is highly competitive with medium-sized, multi-user systems. The system software is based on a previously described system which acquires data from a single gas chromatograph and simultaneously performs statistical analysis for noise compensation, start-of-peak detection, end-of-peak detection, peak area integration, baseline skew, and scale factor corrections. The maximum sampling rate with the Intel 8008 central processing unit (CPU) is 20 Hz, so that 10 gas chromatographic signals can be simultaneously handled with a sampling rate of 2 Hz for each. The corresponding sampling rate for the Intel 8008 CPU is 2 Hz, which limits this CPU to simultaneous control of two gas chromatographs with a sampling rate of 1 Hz for each.

* Abstracted from LBL-4139.

1. L. F. Donaghey, G. M. Bobba and D. Jacobs, *J. Chromatographic Sci.* **14**, 274 (1976).

d. Real-Time Analysis of Gas Chromatograms with a Microcomputer System*

G. M. Bobba and L. F. Donaghey

The real-time performance of a microcomputer system designed for dedicated control of gas chromatography and real-time analysis was studied to determine operating characteristics and accuracy of the peak-area integration algorithm. The software program developed to obtain peak areas used statistical criteria for the detection of the start, maximum value, and end of a chromatographic peak. The accuracy of the system was tested with propane-helium mixtures and by comparison to results obtained with off-line data reduction. The study showed that the real-time microcomputer system gave peak areas which were lower than the off-line results by less than 0.6 percent. The difference was shown to arise from truncation error in the double-precision octal mathematical subroutines, and to error in the assignment of a baseline at the peak end.

* Abstracted from LBL-5411.

e. Decision-Making with Flags in Process Control*

Lee F. Donaghey, G. Mario Bobba, and X. Kim Rubin

Control flags are a powerful component of the instruction sets of many microcomputers. The flags provide the process control programmer with multiple capabilities for conditional branching in microcomputer programs. The uses and applications of the control flags--carry, zero sign and parity--in conditionally braced programs are examined, and useful examples are given for developing programs for the Intel 8008-based microcomputer.

* Abstracted from LBL-3981.

8. RESEARCH PLANS FOR CALENDAR YEAR 1977

Lee F. Donaghey

Studies of the chemical vapor deposition of large-grained GaAs thin film on low-cost substrates will be studied with the objective of improving the efficiency of polycrystalline GaAs solar cells. Theoretical analyses of the effects of thermal cycling and process rate transitions will be initiated to predict methods of grain size enhancement in polycrystalline GaAs layers.

The emission spectra of reactive sputtering plasmas will be studied to determine plasma species formed during the reactive sputtering of titanium by gaseous mixtures of argon, acetylene, methane, and nitrogen.

Study of the systematics of the thermodynamic properties of the Ga-In-Sb system will be undertaken to develop improved methods of tie-line prediction in multi-component systems. Solid-state electrochemical studies will be extended

using CaF_2 electrolytes for determining activity coefficients in the Ga-Al-As system.

The chemical vapor deposition of silicon will be studied both theoretically and experimentally to determine the kinetics of the deposition reaction from SiH_4 and from SiCl_4 . A joint program with John S. Newman is under way to model the deposition process on a heated, rotating disk. A joint program with industry is in progress to explore low-pressure chemical vapor deposition processes.

Manuscripts are in preparation on the following topics:

1. Effect of Surface Treatments on the Nucleation of GaAs on Molybdenum.
2. Chemical Vapor Deposition of GaAs on Au Films.
3. Vapor Phase Etching Kinetics of GaAs.
4. Vapor Phase Etching Kinetics of GaP.
5. Divergent X-ray Diffraction Studies of Ternary and Quaternary Heteroepitaxial Layers.
6. Solidification Kinetics of Cyclohexane.
7. Solidification Kinetics of the Cd-In-Sn Ternary Laminar Eutectic.
8. Thermodynamic Properties of GaSb-InSb System.
9. Study of Factors Affecting Reactive Sputtering Rate Transitions.
10. Reactive Sputter Deposition and Properties of Titanium Carbonitride Films.
11. Erosion Properties of Titanium Carbonitride Films.

9. 1976 PUBLICATIONS AND REPORTS

Lee F. Donaghey and Associates

Journals

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2. G. Mario Bobba and L. F. Donaghey, A Microcomputer System for Analysis and Control of Multiple Gas Chromatographs, *American Laboratory* **8**, 27 (1976).
3. Lee F. Donaghey, Microcomputer Systems for Chemical Process Control, *Proc. IEEE* **64**, 975 (1976).
4. L. F. Donaghey, G. M. Bobba and D. Jacobs, A Microcomputer System for Real-Time Monitoring and Control of Gas Chromatographs, *J. Chromatographic Sci.* **14**, 274 (1976).
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7. B. A. Marmaduke and L. F. Donaghey, Engineering Evaluation of Solid Transition-Metal Sulfide Electrodes for Use in High Energy-Density Batteries, Proc. 11th Intersociety Energy Conversion Engineering Conference, Sept. 12-17, 1976, State Line, Nevada, p. 467.

8. L. F. Donaghey, G. M. Bobba and X. K. Rubin, Decision-Making with Flags in Process Control, Computer Design, 77-83 (1976).

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1. L. F. Donaghey, A Microcomputer System for Real-Time Monitoring and Control of Gas Chromatography, (invited paper), American Chemical Society Centennial Meeting, New York, April 6-8, 1976.

2. K. G. Geraghty and L. F. Donaghey, Effect of Target Oxidation on Reactive Sputtering Rates of Titanium in Argon-Oxygen Plasmas, International Conference on Metallurgical Coatings, San Francisco, April 5-9, 1976.

3. A. L. Lin and L. F. Donaghey, Pseudo-Kossel X-ray Diffraction Studies of Lattice Perfection in LPE-Grown Epitaxial Layers, Paper 61, 149th Meeting of the Electrochemical Society, Washington, D.C., May 2-7, 1976.

4. C. W. Manke and L. F. Donaghey, Analysis of Transport Processes in Vertical Cylinder Epitaxy Reactors, Paper 101, 149th Meeting of the Electrochemical Society, Washington, D.C., May 2-7, 1976.

5. R. H. Bissinger and L. F. Donaghey, Vapor Phase Etching Kinetics of (100) GaAs in HCl-H₂, Paper 120, 149th Meeting of the Electrochemical Society, Washington, D.C., May 2-7, 1976.

6. L. F. Donaghey, Optimization of a Metal-Porcelain Systems for Application in Prosthetic Dentistry, (invited paper, in German), Conference of the Arbeitsgemeinschaft, "Dental Technology," Stuttgart, Germany, June 18, 1976.

7. B. A. Marmaduke and L. F. Donaghey, Engineering Evaluation of Solid Transition-Metal Sulfide Electrodes for Use in High Energy-Density Batteries, 11th Intersociety Energy Conversion Engineering Conference, State Line, Nevada, Sept. 12-17, 1976.

8. C. Figueroa and L. F. Donaghey, Vaporization Kinetics and Vapor Phase Etching Kinetics of (100) GaP in H₂-HCl-PH₃, Paper 233, 150th Meeting of the Electrochemical Society, Las Vegas, Nevada, October 19, 1976.

9. R. de Bernardy and L. F. Donaghey, Chemical Vapor Deposition of GaAs for Solar Cell Applications, Paper 252, 150th Meeting of the Electrochemical Society, Las Vegas, Nevada, October 20, 1976.

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Rolf H. Muller, Principal Investigator

a. Interfacial Concentration in Forced Convection

b. Accumulation of Supporting Electrolyte

Craig G. Smith and Rolf H. Muller

Supporting electrolytes are employed in electrolysis to increase conductivity and reduce migration effects. Near the surface of a working electrode two concentration profiles develop, one for the reacting electrolyte, the other for the supporting electrolyte. Although the supporting electrolyte does not react, it affects electrode processes by altering the chemical environment at the electrode surface.

Ellipsometry has been used to determine interfacial refractive index in the cathodic deposition of Cu from stagnant solutions of 0.1, 0.25 and 0.5 M CuSO_4 with 0.5 - 6 M H_2SO_4 as supporting electrolyte. At the limiting current Cu^{++} concentration at the electrode surface is zero and the refractive index is determined exclusively by the H_2SO_4 concentration. Results given in Fig. 2 show an increase in sulfuric acid concentration of up to 20%; the maximum in the curves is due to the partial dissociation of H_2SO_4 . The measurements are in good agreement with earlier predictions.^{1,2}

Fig. 2. Accumulation of supporting electrolyte at the interface. Cu deposition from $\text{CuSO}_4 - \text{H}_2\text{SO}_4$ mixtures, stagnant solution, limiting current.
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c. Correction of Component Imperfections of the Automatic Ellipsometer

Craig G. Smith, Janet S. Remer and Rolf H. Muller

The components of the optical train of ellipsometers generally contain optical imperfections such as strain-induced birefringence, dichroism or misalignment of azimuth circles. Such imperfections are recognized by differences in results obtained in different zones. The increased number of optical components employed in automatic ellipsometers and the use of sealed windows in vacuum chambers make it particularly desirable to account for errors caused by imperfect components. A previous analysis for a manually operated ellipsometer¹ has been extended to include the Faraday cells in our self-compensating instrument.

In the analysis a matrix notation² is used to represent the optical effect of individual components, and matrix multiplications relate the sequential effect of the components on the transmitted light. Imperfections are treated as first order Taylor series expansions about the ideal component values. The glass cores of the Faraday cells are assumed to be birefringent and dichroic to produce both relative phase and relative attenuation effects. In a calibration process 24 measurements are performed from which 19 imperfection parameters have to be computed.

The magnitude of the corrections involved for our automatic ellipsometer³ is shown in Fig. 3.

Fig. 3. Effect of component imperfections on the derivation of relative attenuation ψ and relative phase Δ from ellipsometer measurements. Dissolution of Zn single crystal (1000) at constant potential (-1.0 V vs. Hg/HgO) in stagnant KOH. (XBL 7611-9910)

Experimental observations on the anodic dissolution at constant potential of zinc in 0.5 M KOH are interpreted under the assumption of ideal components and by considering component imperfections. The corrected curve is translated by about three degrees in ψ and about one degree in Δ from the uncorrected curve. Over a larger range of measured parameters the magnitude of the correction is not constant and may even change sign.

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2. LASER VELOCIMETRY FOR ELECTROCHEMICAL BOUNDARY LAYERS*

Calvin T. Chew and Rolf H. Muller

A laser Doppler velocimeter that operates sequentially in the reference mode and two differential modes, and which provides three orthogonal velocity components in boundary layers, has been further developed. The probe volume for differential operation is an ellipsoid of $20 \times 19 \times 68$ microns; for reference operation it is a truncated ellipsoid of 11×230 microns.

The use of backscattered light for the measurements has greatly simplified corrections for light deflection in boundary layers. Backscattered light intensities from dielectric suspended particles are, however, very low. For this reason, and because of the low difference frequencies to be observed (4 kHz for 1 cm/sec) signal-to-noise ratios obtained have been poor. In addition to the use of metallized scattering particles, an electronic spectrum analyzer that is less wasteful of signal will be needed for satisfactory operation.

* Abstract of M.S. thesis by Calvin T. Chew, Laser Velocimetry with High Spatial Resolution, LBL-5725, September 1976.

3. OPTICAL INTERFERENCE IN ELECTROLYTE FILMS

Michael L. Sand and Rolf H. Muller

A further removal of solid particles from filtered KOH solutions has been accomplished by fractional crystallization at reduced temperature. The resulting solutions have produced liquid films that continue thinning on vertical metal surfaces for longer periods than observed previously with more contaminated solution. The effect of the residual roughness of optically polished Pt electrodes on film stability still needs to be explained.

Principles of interference color analysis and the concept of an optimum angle of incidence based on color purity have been summarized in an 8-min-long movie. Computer-generated spectra and chromaticity plots are compared to experimental observations for substrates of intermediate (Cr) and high (Al) reflectivities.

4. INTERFEROMETRY OF MASS-TRANSFER BOUNDARY LAYERS

Karrie J. Hanson, Rolf H. Muller and Charles W. Tobias

A major limitation to the industrial implementation of electrochemical technology is the low mass transfer rate associated with electrochemical processes. For this reason, methods to increase mass transfer in electrochemical cells have continuing significance. Preliminary interferometry studies¹ have indicated that turbulence promoters² in electrochemical flow cells have the effect of thinning mass-transfer boundary layers and substantially increasing rates of mass transfer to the surface. Interferometry is a particularly useful technique for these studies because it allows direct visualization of the mass-transfer boundary layer and it can be used below limiting current. Initial studies will be directed towards establishing obstacle shapes and spacings which produce the maximum turbulence in the boundary with the minimum increase in pressure drop.

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5. RESEARCH PLANS FOR CALENDAR YEAR 1977

Rolf H. Muller

The concentration of supporting electrolyte at an electrode surface will be determined experimentally for forced convection mass transport by the use of ellipsometry. Theoretical predictions of the accumulation of supporting electrolyte, which can affect the electrocrystallization of metals, have not been compared to experiment for these conditions.

The dynamic range of the automatic ellipsometer, presently 55° for polarizer and analyzer azimuths, will be doubled in order to follow larger surface changes without mechanical adjustment. The introduction of rapid-scanning spectroscopic ellipsometry for the identification of transient surface compounds, which will require on-line digital data handling capabilities, is planned.

Means for the acceleration of ionic mass transport by boundary layer tripping will be investigated by interferometry. Shapes and spacings of flow obstacles which reduce the boundary layer thickness with the least increase in pressure drop will be investigated.

6. 1976 PUBLICATIONS AND REPORTS

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e. Solid State and Surface Reaction Studies. Surface Science and Heterogeneous Catalysis

Gabor A. Somorjai, *Principal Investigator*

1. SURFACE STRUCTURE AND CHEMISORPTION BY LOW ENERGY ELECTRON DIFFRACTION

a. LEED Intensities of Hydrocarbons Adsorbed on the Pt(111) Surface

Peter C. Stair and Gabor A. Somorjai

The intensities of the low-energy electron diffraction beams backscattered from the ordered (2x2) overlayers of acetylene, methylacetylene, ethylene and propylene on the platinum (111) crystal face were measured by a photographic technique. The intensities were recorded in the form of normalized diffraction beam-intensity vs. incident-electron-energy (I-V curves). Acetylene, methylacetylene and propylene spontaneously form the ordered (2x2) adsorbate structure on platinum at 300 K and at low exposures under ultrahigh vacuum conditions. For acetylene and methylacetylene the intensity profiles reveal that this structure is metastable and upon heating to 350-400 K for 1 hour, both hydrocarbons undergo a transformation to a stable structure with the same (2x2) unit cell size. The intensity profiles strongly suggest that the structural nature of the transformation is very similar for both molecules, and that it involves a strengthening of the carbon-platinum bond accompanied by an expansion of the unsaturated carbon-carbon bond length.

Ethylene adsorbs on the platinum (111) surface and with electron beam exposure forms an ordered (2x2) surface structure. The intensity profiles from the ordered ethylene and propylene indicate that their structures are identical to the stable acetylene and methylacetylene structures respectively. Thus, ethylene dehydrogenates to acetylene and propylene to methylacetylene upon adsorption on the Pt(111) surface.

b. The Surface Structure and Bonding of (2x2) Acetylene Overlayers on Platinum (111): LEED Intensity Analysis

Larry L. Kesmodel, Roger C. Baetzold,* and Gabor A. Somorjai

The stereochemistry of C_2H_2 on single-crystal Pt(111) surfaces has been elucidated by means of dynamical low-energy electron diffraction (LEED) calculations with comparison to the experimental data of Stair and Somorjai.¹ The stable form of chemisorbed C_2H_2 is found to be in a triangular bonding configuration (Fig. 1) at a distance of 1.95 ± 0.01 Å above the platinum surface, C-Pt distances of 2.2 Å and 2.6 Å are found. Although the calculations are relatively insensitive to the degree of surface-induced C-C bond lengthening, preliminary analysis of the hydrogen positions indicates that the CCH bond angles are greater than 190° . Thus, rehybridization from sp to sp^2 electronic configuration is not complete. The triangular mode of bonding we find on the Pt(111) surface seems qualitatively related to that found

Fig. 1. Probable bonding arrangement for acetylene on the Pt(111) surface and the stable adsorption state. (XBL 7611-4438)

in trinuclear metal-alkyne complexes. Work is in progress to better define the degree of CCH bending and to examine the bonding of methylacetylene on the Pt(111) surface.

*Visiting scientist from Eastman-Kodak Laboratories, Rochester, New York.

1. P. C. Stair and G. A. Somorjai, LBL-5421 (J. Chem. Phys. to be published.)

c. Surface Structures of Normal Paraffins and Cyclohexane Monolayers and Thin Crystals Grown on the (111) Crystal Face of Platinum. A LEED Study

L. E. Firment and Gabor A. Somorjai

The surfaces of the normal paraffins (C_3 - C_8) and cyclohexane have been studied using low-energy electron diffraction (LEED). The samples were prepared by vapor deposition on the (111) face of a platinum single crystal in ultrahigh vacuum, and were studied both as thick films and as adsorbed monolayers. These molecules form ordered monolayers on the clean metal surface in the temperature range 100 to 220 K and at a vapor flux corresponding to 10^{-7} Torr. In the adsorbed monolayers of the normal paraffins (C_4 - C_8), the molecules lie with their chain axes parallel to the Pt surface and $Pt[1\bar{1}0]$. The paraffin monolayer structures undergo order-disorder transitions as a function of temperature. Multilayers condensed upon the ordered monolayers maintained the same orientation and packing as found in the monolayers. The surface structures of the growing organic crystals do not correspond to planes in the reported bulk crystal structures and there is evidence for epitaxial growth of pseudomorphic crystal forms. Multilayers of n-octane and n-heptane condensed upon disordered monolayers have also grown with the (001) plane of the triclinic bulk crystal structures parallel

to the surface. n-Butane has three monolayer structures on Pt(111) and one of the three is maintained during growth of the crystal. Cyclohexane forms an ordered monolayer, upon which a multilayer of cyclohexane grows exhibiting the (001) surface orientation of the monoclinic bulk crystal structure. Surface structures of saturated hydrocarbons are found to be very susceptible to electron beam induced damage. Surface charging interferes with LEED only at sample thicknesses greater than 200 Å.

d. LEED Studies of Amino Acids on Cu Crystal Surfaces

Jeffrey C. Buchholz, Ljiljana Atanasoska,* and Gabor A. Somorjai

LEED studies have been carried out on monolayer and multilayer deposits of amino acids on clean copper single crystals of (111) and (100) orientation. The amino acids studied were: glycine, L-alanine, L-tryptophan, D-tryptophan and DL-tryptophan. Each of these were deposited by subliming commercial amino acid powder at 200°C onto the substrates which had been cleaned and previously characterized with LEED and Auger spectroscopy.

Glycine was found to adsorb on both Cu(111) and Cu(100). On Cu(111) an ordered (8×8) monolayer structure was formed. At low coverages on Cu(100) a streaked diffraction pattern is produced. With increased coverage additional ordering takes place as evidenced by a gradual contraction of the streaks into spots. Glycine does not grow into a thick layer on either crystal face.

L-alanine also forms ordered monolayer structures on both Cu(111) and Cu(100) crystal faces. Multilayer deposits of L-alanine were observed but these surfaces were not ordered.

L-tryptophan forms both monolayer and multilayer ordered structures on both Cu(100) and Cu(111) and the structures are substrate dependent. On both substrates the surface unit cell changes dramatically on going from the monolayer to the multilayer regime. The analysis of these diffraction patterns for determining the size and shape of the unit cells is in progress.

Experiments are in progress on D-tryptophan and on the racemic DL-mixture. Preliminary results suggest that D-tryptophan and L-tryptophan may form different ordered structures in both the monolayer and multilayer on Cu(111). On Cu(100), they form different ordered structures in the monolayer, but the same one in the multilayer. The DL mixture does not order in the monolayer but does order in the multilayer on both substrates.

Electron beam damage effects for the energies and beam exposures used in these experiments vary significantly with the molecule and substrate under study. We are studying the conditions necessary to minimize this damage.

The effect of substrate temperature on the ordering of these layers was also investigated but no temperature dependence was observed.

Similar studies will be applied to other biologically important bases in nucleic acids.

* Graduate student at the Center for Multidisciplinary Studies of the University of Belgrade, Yugoslavia.

e. Chemisorption on Rh(100) and Rh(111) Surfaces

David Kastner, Brett Sexton, and Gabor A. Somorjai

Although rhodium is one of the more important heterogeneous catalysts for the hydrogenation and insertion reactions, it is one of the least-studied metals in terms of fundamental characterization of its surface structure and chemisorption properties. The Rh(100) and (111) surfaces have been prepared and characterized in that clean state in ultrahigh vacuum, with LEED and Auger spectroscopy. The clean surfaces are unreconstructed and exhibit high reactivity towards adsorption of gases. Ordered surface structures have been observed for NO, CO, O₂, C₂H₂, C₂H₄, B, S and C on both surfaces. Hydrogen adsorbs but does not alter the clean surface LEED patterns. Temperature programmed desorption of the adsorbed layers has been carried out and the activation energies and descriptive orders have been tabulated.

f. Low-Energy Electron Diffraction Studies of the Clean (110) and (111) Crystal Faces of Iron and of the Chemisorption of Carbon Monoxide and Acetylene

K. Yoshida and G. A. Somorjai

LEED studies of chemisorption of CO and C₂H₂ on (110) and (111) crystal faces of iron were carried out in the reactant pressure range of 10⁻⁹ to 10⁻⁵ Torr, and at surface temperature of 300 to 900 K. The (110) surface has the same (1×1) structure as expected from the projection of the bulk unit cell, but the (111) surface appears to be reconstructed and has a (4×4) surface structure that appears only after repeated argon ion-bombardment and high-temperature anneal.

C₂H₂ and CO adsorb at all conditions of the experiment on these two crystal faces. Adsorption of CO on the (110) crystal surface results in a streaky pattern where lines become visible in the [001] direction between the diffraction beams characteristic of the clean iron surface. With increased pressure, p(1×1) and p(2×1) surface structures appear. However, on heating to 650 K, the LEED pattern that appears to be characteristic of a carbon structure was observed. C₂H₂ adsorbs readily on the (110) crystal face and all diffraction features disappear using an exposure of 6×10⁻⁷ Torr sec. It appears that the iron surface disorders in the presence of the adsorbate. On flashing to 900 K, a new surface structure appears that is characteristic of a carbon structure that is also observed on heating the surface after CO adsorption to 650 K. CO and C₂H₂ adsorptions on the (4×4) surface structure of the (111) crystal face at 300 K result in the formation of a (1×1) surface

structure. On flashing to higher temperature after adsorption, a diffuse carbon pattern is observed.

g. A LEED and AES Study of the Structure, Debye Temperature and Oxidation of the (111) Crystal Face of Thorium

R. Bastasz, C. A. Colmenares, R. L. Smith, and Gabor A. Somorjai

The structure and reactivity towards O_2 and CO , of the (111) crystal face of a single crystal of high purity thorium metal was studied using low-energy electron diffraction (LEED) and Auger electron spectroscopy. The sample was cleaned in vacuum by a combination of ion bombardment and annealing. Extended annealing of the cleaned sample at 1000 K produced a new LEED pattern characteristic of a (9×9) surface structure. A model of a reconstructed thorium surface is presented which would generate the observed LEED pattern. In this model an α and β thorium phase transformation at the surface, which occurs at a lower temperature than the corresponding phase transformation in the bulk, is the case of the surface reconstruction. When monolayer amounts of either O_2 or CO were adsorbed onto the crystal surface at room temperature, no ordered surface structures formed. Upon heating the sample following these exposures the (111) surface structure was restored accompanied by a reduction in the amount of surface carbon and oxygen. With continued exposure to either O_2 or CO and annealing, a new LEED pattern developed which was interpreted as resulting from the formation of thorium dioxide. Debye-Waller factor measurements were made by monitoring the intensity of a specularly reflected electron beam and indicated that the Debye temperature of the surface region is less than it is in bulk thorium. Consequently, the mean displacement of thorium atoms from their equilibrium positions was found to increase at the surface of the crystal. The presence of chemisorbed oxygen on the surface influenced the Debye temperature, raising it significantly.

h. Surface Structures and Chemical Compositions of TiO_2 (Rutile) Single Crystals

Y-W. Chung, W-J. Lo, and Gabor A. Somorjai

Low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) have been used to study the surface geometric structures and chemical compositions of titanium dioxide single crystal with rutile structure which is tetragonal with $a=b=4.59$ Å and $c=2.96$ Å. Three different surfaces with (001), (110) and (100) orientations have been studied. The surfaces were cleaned by Ar ion sputtering and ordered by heating the crystal above 600°C in the ion-pumped stainless steel vacuum system with base pressure 1×10^{-10} Torr. LEED studies show that these crystal surfaces with different orientations behave differently in ultrahigh vacuum conditions. The (001) and (100) facets. While the (110) surface remains a stable (1×1) unreconstructed structure. In contrast to the (001) and (110) surface, the (100) surface reconstructs along the a -axis. LEED patterns show three distinct structures.

The (3×1) -(100) structure appears at annealing temperature 600°C. On raising the temperature to 800°C, the surface transforms to the second structure with (5×1) -(100) LEED pattern. Finally, we observe a (7×1) -(100) LEED diffraction pattern by heating the crystal to 1200°C.

The surface stoichiometry was monitored by measuring the peak ratio of oxygen (510 eV) to titanium (380 eV) in the Auger electron spectrum. We observed large variations of this ratio for different surface conditions. It varies from 1.7 for clean ordered (1×1) -(110) surface to 1.3 after Ar ion bombarding this surface which is due to the preferential sputtering of oxygen from the surface. The same decrease of this ratio from 1.7 to 1.3 occurs in the Auger electron spectra which correspond to (3×1) , (5×1) and (7×1) -(100) surface structure respectively.

This suggests that there is a close correlation between the surface structures seen by LEED and surface compositions determined by AES. The successive transformations of surface structure from (3×1) -(100) to (7×1) -(100) seen by LEED results from the loss of oxygen from the surface by heating and thus decreases the surface concentration of oxygen shown in the AES.

i. Theory of the Structure of Acetylene Chemisorbed on a Platinum (111) Surface*

Roger C. Baetzold,[†] Larry L. Kesmodel, and Leo M. Falicov

We have applied a semi-empirical extended Hückel calculation to the bonding of C_2H_2 on a 9-atom platinum cluster chosen to model the platinum (111) surface. Using realistic geometries obtained from LEED,¹ we have studied CCH bond-angle distortion, molecular orbital energies and changes in the π_u vibrational modes. Results are presented with and without charge iteration, and it is found that predicted CCH angle bending is very sensitive to the degree of charge transfer from the molecule to the surface. Sizeable splitting (~ 1 eV) of the degenerate $1\pi_u$ orbitals is predicted for the case of large surface-induced (40° - 60°) CCH angle bending.

*Abstracted from LBL-5157, submitted to J. Chem. Phys.

[†]Visiting scientist from Eastman-Kodak Laboratories, Rochester, New York.

1. L. L. Kesmodel, R. C. Baetzold and G. A. Somorjai, LBL-5407, submitted to J. Chem. Phys.

j. Phenomenological Theory of the Activation Energy of Hydrocarbon on Catalytic Stepped Platinum Surfaces*

Y. W. Tsang and Leo M. Falicov

A phenomenological theory* has been constructed which allows calculation of the heat of formation and activation energy of C-H, C-C and H-H bond scission processes on stepped platinum surfaces.

The dependence of these energies on the location of the active platinum atom has been studied and is in agreement with trends found experimentally. Catalytic properties of steps and kinks can therefore be attributed to the local field properties of the platinum d-electrons.

* Abstracted from LBL report, submitted to J. Catalysis.

2. ELECTRON SPECTROSCOPY STUDIES OF SOLID SURFACES AND ADSORBATES

a. The Surface Composition of Au-Sn Alloys Determined by Auger Electron Spectroscopy

S. Overbury and Gabor A. Somorjai

The Auger spectra of clean and equilibrated Au-Sn alloy ingots of bulk composition ranging between 50 and 99 at.% Au have been obtained. The intensity ratios of Auger peaks of various different energies were normalized by comparison with the corresponding intensity ratios from pure Au and Sn. The normalized intensity ratios are used to obtain the surface atom fractions by applying a model which takes full account of the attenuation of the Auger electrons. It is found that for a one phase alloy with overall composition of 50 at.% Au there is little or no segregation at the surface, while for a one phase alloy with bulk composition of 86 at.% Au there is marked segregation of Sn (surface monolayer composition of about 53 at.% Au). For the alloys of bulk compositions between 50 and 86 at.% in which both phases are present, the surface composition is given by applying the lever rule to the one phase surface compositions. For 1 at.% Sn dissolved in the Au lattice there is also considerable enrichment of the surface with Sn (surface monolayer composition of about 46 at.% Au). These surface compositions are related to the properties of the bulk phase diagram and are explained by the interplay of the differences in atomic size and in heats of sublimation of pure Au and Sn and of the heats of mixing of the alloys.

b. The Surface Composition of the Gold-Palladium Binary Alloy System

Aleksander Jablonski, S. Overbury, and Gabor A. Somorjai

The surface composition of the AuPd alloy system has been determined by Auger electron spectroscopy. Measurements were performed on polished polycrystalline alloy foils. After cleaning, the intensities of the 71 eV and 2024 eV gold Auger transitions, and the intensity of the 330 eV palladium transition were measured, and then converted to atom concentrations in the surface layer. The surfaces of the annealed samples were found to be significantly enriched in gold with respect to the bulk. This result disagrees with the regular solution theory prediction. After extensive sputtering of the AuPd alloys with 1.5 keV Ar⁺ ions, a slight

surface enrichment with palladium was found, as predicted by the simple theoretical model for sputtering.

c. Electron Spectroscopy Studies of Clean (110) and (100) Titanium Dioxide (Rutile) Single Crystal Surfaces

Y-W. Chung, W-J. Lo, and Gabor A. Somorjai

Low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), electron energy loss (ELS) and ultraviolet photoemission spectroscopies (UPS) were used to study the structures, compositions and electron state distributions of clean single crystal faces of titanium dioxide (rutile). LEED showed that both the (110) and (100) surfaces are stable, the latter giving rise to three distinct surface structures, viz. (1×3), (1×5) and (1×7), that were obtained by annealing an argon ion-bombarded (100) surface at ~600, 800 and 1200°C respectively. AES showed the decrease of the O(510 eV)/Ti(380 eV) peak ratio from ~1.7 to ~1.3 in going from the (1×3) to the (1×7) surface structure. Electron energy loss spectra obtained from the (110) and (100)-(1×3) surfaces are similar, with surface-sensitive transitions at 8.2, 5.2 and 2.4 eV. The energy loss spectrum from an argon or oxygen ion bombarded surface is dominated by the transition at 1.6 eV. UPS indicated that the initial state for this ELS transition is peaked at -0.6 eV (referred to the Fermi level E_F) in the photoemission spectrum, and that the 2.4 eV surface-sensitive ELS transition probably arises from the band of occupied states between the bulk valence band maximum to the Fermi level. High energy electron beams (1.6 keV 20 μA) used in AES were found to disorder clean and initially well-ordered TiO₂ surfaces. Argon ion bombardment of clean ordered TiO₂ (110) and (100)-(1×3) surfaces caused the work function and surface band bending to decrease by almost 1 eV and such decrease is explained as due to the loss of oxygen from the surface.

d. Electron Induced Luminescence as a Technique for Studying Oxygen Adsorption on Thorium

R. J. Bastasz, C. A. Colmenares, R. L. Smith, and Gabor A. Somorjai

When an electron beam strikes a sample of thorium metal, a blue luminescence can be observed. The intensity of this luminescence is affected by gases adsorbed on the sample surface and this phenomenon has been used to study the mechanism of oxygen adsorption on thorium. A high purity thorium sample, after being cleaned in vacuum by a combination of argon ion bombardment and high temperature annealing, was exposed to a low pressure (10 μPa) of oxygen while its luminescence intensity in a 3 keV electron beam was measured. In addition, Auger electron spectroscopy (AES) measurements of the thorium sample were made during oxygen exposure and by considering both the luminescence and AES data, it was possible to distinguish two processes involving adsorbed oxygen that produced luminescence. One process associated with luminescence is dependent upon the oxygen pressure at the sample surface while the other process is

dependent only upon the amount of adsorbed oxygen. These two findings correlate with a mechanism for oxygen adsorption on thorium in which gas phase oxygen is adsorbed followed by irreversible dissociation of molecular oxygen at the surface into monatomic chemisorbed oxygen, which leads to the formation of ThO_2 . In this mechanism, the oxygen pressure dependence of the luminescence intensity arises from a process involving adsorbed molecular oxygen and the dependence of the luminescence intensity upon the amount of adsorbed oxygen arises from a process involving monatomic chemisorbed oxygen.

3. MOLECULAR BEAM-SURFACE INTERACTIONS

a. Molecular Beam Investigation of the H_2 - D_2 Exchange Reaction on Platinum Single Crystal Surfaces

R. Gale, M. Salmeron and G. A. Somorjai

The dependence of the reaction probability for H_2 - D_2 exchange on angle of incidence and azimuthal angle has been studied on two stepped surfaces, $\text{Pt}(S)$ -[5(111) $\times$ (111)] and $\text{Pt}(S)$ -[6(111) $\times$ (111)] and on the $\text{Pt}(111)$ surface. The azimuthal angle is varied by rotating the crystal around its center. We designate $\phi=90$ when the open edge of the step is facing away from the beam (antiperpendicular). The angle of incidence is measured from the macroscopic surface normal.

On the stepped surfaces, the reaction probability exhibits a marked dependence on the orientation of the steps with respect to the incident beam. As the azimuthal angle is varied from $\phi=0$ to $\phi=90$, with an angle of incidence of 45° , the production of HD is found to increase by $\sim 50\%$ under a wide variety of conditions, i.e., high and low modulation frequencies, using a mixed beam or one reactant in the beam and the other in the background, for surface temperature ranging from 800 K to 1400 K. For low modulation frequencies and surface temperatures in this range, the reaction probability exhibits a similar trend, increasing by $\sim 50\%$ as the azimuthal angle is varied from $\phi=90$ to $\phi=0$.

The production of HD is also found to depend significantly on the angle of incidence of the beam on the stepped surfaces. At low modulation frequency, with the step edge perpendicular to the incoming beam, a steady increase in HD formation is found. As the angle of incidence is varied from grazing angles with the open edge of the step directed away from the beam to grazing angles with the open edge of the step toward the beam, an increase of approximately a factor of two from $\sigma=-60$ to $\sigma=60$ is found. No dependence on angle of incidence or azimuthal angle is found for the reaction on the $\text{Pt}(111)$ surface.

These results indicate that the higher reaction probability found on the stepped surfaces is associated with the area between the step edge and the terrace, due to a higher probability of energy exchange at these sites enhancing the dissociative adsorption of the reactants.

b. Construction of a Molecular Beam-Surface Scattering Apparatus for Reaction Kinetics Analysis and Velocity Analysis

S. T. Ceyer, W. T. Siekhaus, Y. T. Lee, and Gabor A. Somorjai

A surface scattering apparatus has been designed and is presently being constructed which will enable the study of catalytic surface reaction mechanisms and the translational velocity of the scattered particles from the surface. The latter feature is an important measurement for a detailed understanding of the energy exchange process between a gaseous species and a solid surface.

The apparatus consists of several independently pumped chambers; two source chambers each with their differential pumping chamber, the ultrahigh vacuum scattering chamber and the detector unit which houses a mass spectrometer in one chamber and its differential pumping chamber. The differential pumping of the source and detector are necessary to achieve ultrahigh vacuum conditions in the scattering chamber and to achieve a high signal-to-noise ratio at the detector. The detector unit rotates in the main scattering chamber by a mechanical coupling to the outside so that an angular distribution of particles scattered from a surface can be investigated. There are double walls on the detector unit which can be filled with liquid nitrogen for cryopumping. Mounted on the detector unit is a cross correlation chopper and motor for time-of-flight analysis as a function of scattering angle. A similar chopper and motor are mounted on the source chamber to modulate the incident beam for reaction mechanism studies.

LEED and Auger electron spectroscopy are used for surface characterization. These facilities are not at the scattering center so that a device for surface manipulation was designed. The designed manipulator has three degrees of translational motion, two degrees of rotation and a tilt mechanism. The latter degrees of freedom allow for angle of incidence variation, variation of the orientation of surface microstructure with respect to the incident beam and observation of out of plane scattering, respectively.

4. STUDIES OF CATALYZED SURFACE REACTIONS

a. Hydrogenation of Cyclohexane and Dehydrocyclization of n-Heptane Over Single Crystal Surfaces of Iridium

B. E. Nieuwenhuys and Gabor A. Somorjai

The dehydrogenation of cyclohexane and the dehydrocyclization of n-heptane were investigated at low hydrocarbon pressure ($\sim 10^{-5}$ Torr) on two single crystal surfaces of iridium. The surfaces studied were $\text{Ir}(111)$ and $\text{Ir}(755)$ or stepped [6(111) $\times$ (100)]. The reaction rates were monitored by a quadrupole mass spectrometer, the surface structure and surface composition were determined by means of low-energy electron

diffraction and Auger electron spectroscopy. The results are discussed and compared with similar studies on single crystal surfaces of platinum. The stepped iridium surface appeared to be a factor of 5 more active in dehydrogenation than the iridium (111) surface. The activity of iridium in dehydrocyclization was lower than that for platinum surfaces of the same structure.

b. Pre-Exponential Factors in Surface Reactions

R. C. Baetzold* and Gabor A. Somorjai

Pre-exponential factors for surface reactions have been estimated by use of transition state and hard sphere reaction models. We find that calculated values can be used to determine rate limited steps in various surface reactions. In the case of H₂-D₂ exchange, adsorption is the rate limiting step at high temperature while bond breakage becomes rate limiting at low temperature. Typical pseudo-first order pre-exponential factors for various rate limiting steps are: adsorption 10^2 - 10^4 sec⁻¹, diffusion 10^7 - 10^{11} sec⁻¹, surface reaction 10^{10} - 10^{15} sec⁻¹, desorption 10^{13} - 10^{16} sec⁻¹. The calculated values are compared to numerous examples of surface reactions compiled from the literature. In addition, conditions needed to apply these models to catalyzed reactions are discussed.

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c. Light-Assisted Surface Reactions. The Production of Hydrogen and Oxygen by Water Dissociation on Semiconductor Surfaces

John Hemminger and Gabor A. Somorjai

In this project we explore the surface properties of materials that carry out photon-assisted chemical reactions. These are semiconductors with band gaps of ~2 eV or greater. Among them, TiO₂ and GaP appear to be very promising for the photon-assisted conversion of water to form H₂ and O₂. An electrochemical cell using TiO₂ as the anode and p-type GaP as the cathode was shown to be capable of the electrolysis of water with no external voltage required when the electrodes were irradiated.

Reactions that are catalyzed by surfaces must be thermodynamically feasible. Yet many reactions of great importance like the reactions of H₂O and CO₂ to produce hydrocarbons and oxygen (photosynthesis) or the dissociation of water are not thermodynamically feasible. In this circumstance, light that creates photoelectrons of reasonable lifetimes at the solid surface is used to assist the chemical reaction. The purpose of our studies is to understand the role of the photoelectron in the reactions of water and carbon dioxide. Using this knowledge we should be able to develop materials with suitable surface structure and composition to optimize the photon-assisted reaction rates and product distributions. If energy can be provided by sunlight and efficiently utilized in the course of these reactions, hydrogen and hydrocarbons may be produced.

Well-characterized titanium oxide crystals are being used in our studies to explore the mechanism of adsorption of oxygen, hydrogen and water and the light-assisted dissociation of water on the various crystal surfaces of this material. It is hoped that light-assisted catalytic reactions will play an important role in synthetic fuel production.

d. High Pressure Studies of Catalytic Activity of Platinum Crystal Surfaces

Richard K. Herz, E. E. Petersen, and Gabor A. Somorjai

Crystal faces studied in this work are designated as the (111), (755) and (211) planes in Miller Index notation. The (111) plane of platinum is a flat, close-packed hexagonal array. The (755) surface has terraces of (111) planes with a monatomic step up to another (111) plane every six atoms (on the average). A more descriptive notation for the surface is Pt(S)-[6(111)×(100)], where (S) denotes a stepped surface. Similarly, the (211) surface can be designated Pt(S)-[3(111)×(100)]. It has narrower terraces and a higher step density (by a factor of two) than the [6(111)×(100)] surface.

Studies of two reactions were performed: the dehydrocyclization of n-heptane to toluene, and the dehydrogenation of cyclohexane to benzene. Hydrocarbon pressures were varied between 5 and 80 Torr, hydrogen pressures between 0 and 760 Torr and crystal temperatures between 220 and 325°C.

The (111) surface is active for dehydrocyclization, but is rapidly deactivated by coverage of its flat surface by a disordered carbonaceous overlayer. Step atoms may retain their activity by "sticking out" and not being blocked by the overlayer.

Carbonaceous overlayer deactivation was also present for the dehydrogenation of cyclohexane but to a lesser extent. In this reaction, product inhibition due to the accumulation of benzene in the batch reaction was important. Irreversible deactivation was less than one-third of the reversible benzene inhibition, so data was fit with a first order product inhibition function.

Table 1 lists the specific rates and inhibition parameters for the three surfaces at reaction

Table 1. Cyclohexane → benzene. $R = R_s / (1 + K[\text{benz}])$.

15 Torr cyclohexane			
100 Torr H ₂ :	(111)	[6(111)×(100)]	[3(111)×(100)]
R _s (μmole/min·cm ²)	7.8	0.85-1.1	2.3
K (Torr ⁻¹)	190	4.5-5.0	4.1
300 Torr H ₂ :			
R _s (μmole/min·cm ²)	2.2-2.4		5.9
K (Torr ⁻¹)	3.3-5.2		3.9

conditions of 15 Torr cyclohexane, 100 Torr hydrogen and 300°C. The (111) surface was active for dehydrogenation, but was very susceptible to product inhibition. At these conditions, the inhibition parameter, K , for the flat surface was about 40 times those of the stepped surfaces and was very sensitive to hydrogen pressure: $K \propto [H_2]^{-5}$. A negative order dependence was also observed for the dehydrogenation rate on this surface.

The $[3(111) \times (100)]$ crystal was approximately twice as active as the $[6(111) \times (100)]$. Inhibition parameters on the stepped surfaces were relatively insensitive to hydrogen and dehydrogenation rates increased with hydrogen.

e. The Stability and Structure of High Miller Index Platinum Crystal Surfaces in Vacuum and in the Presence of Adsorbed Carbon and Oxygen

D. W. Blakely and G. A. Somorjai

The surface structures of twenty-two high Miller Index crystal faces of platinum were studied in ultrahigh vacuum (uhv) when clean and in the presence of a monolayer of chemisorbed oxygen or carbon by low-energy electron diffraction (LEED). Besides the low Miller Index planes [the (001), (001) and (111)], only a few of the surfaces [the (112), (113), (133), (122) and (012)] were stable under all conditions of the experiments. The stable surfaces are characterized by a very high density of periodic steps of one atom in height or a complete lack of steps. The other platinum crystal faces restructure as the surface composition is changed. Some of the surface structures that are stable in uhv and in oxygen reconstruct in the presence of carbon while others are stable when clean and when carbon covered but restructure when covered with oxygen. In addition to the one atom high step-terrace configuration there are atomically clean surface structures with multiple height steps and structures in "hill and valley" configuration consisting of large facet planes detectable by LEED.

5. RESEARCH PLANS FOR CALENDAR YEAR 1977

G. A. Somorjai

We shall compare the reactivity of platinum monolayers deposited on inert single crystal substrates with the reactivity of platinum single crystals.

We shall study the structure, composition and reactivity of binary alloy clusters that are formed by controlled deposition from the vapor phase.

The surface crystallography of ethylene and acetylene on rhodium and nickel surfaces will be investigated.

We shall study the surface structure and reactivity of monolayers of metallo-organic compounds.

The photon assisted dissociation of water on gallium phosphide surfaces will be explored.

The distribution of chemical energy during the recombination of hydrogen atoms on solid surfaces will be explored.

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f. Nuclear Magnetism*

Alexander Pines,[†] *Principal Investigator*

1. ^{13}C MAGNETIC SHIELDING IN ORGANOMETALLIC COMPOUNDS

D. E. Wemmer and A. Pines

Shielding tensors for ^{13}C in various organic compounds have proved to be very sensitive probes of local electronic structure and symmetry. One class of organometallic compounds which we have studied are metallocenes. These compounds are interesting because of their unusual bonding, consisting of a metal atom sandwiched between two aromatic rings. While the general nature of the bonding is well understood, quantitative differences among various metals are difficult to characterize and understand. Since the ^{13}C shielding tensor is very sensitive to the local electronic structure, it is particularly suitable to study the metal-aromatic bonding.

Among the compounds we have studied are dicyclopentadienyl complexes of various metals. We find large differences in the width of the shielding tensors for various metals which reflect differences in the covalent vs. ionic character of the bond. Another complex we have

studied is bisbenzene chromium. In this case it is possible to contrast the shielding tensor for the free benzene molecule with its counterpart bound to a chromium atom. Here we find that the anisotropy for the metal bound ring is 34% less than for the free benzene (Fig. 1), an effect that stems solely from the interaction with the metal and which will be important in studying the adsorption of aromatics on metal surfaces.

*Supported in part by the National Science Foundation.

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2. PHASE TRANSITION AND MOLECULAR MOTION IN SOLID PENTAMETHYLBENZENE

D. E. Wemmer and A. Pines

For many years it has been known that pentamethylbenzene exhibits an interesting first order

Fig. 1. Room temperature ^{13}C powder patterns for benzene and bisbenzene chromium, showing changes which occur upon bonding to the metal. The tensors are axially symmetric due to rapid rotation about the C_6 axis. (XBL 771-7395)

Fig. 1. ^{13}C powder patterns for pentamethylbenzene showing the averaging of σ_{11} and σ_{22} elements which occurs above the phase transition at 24°C . (XBL 771-7396)

phase transition, from one crystalline phase to another at 24°C. However, very little work has been done to characterize the phase transition or the molecular changes which accompany it, since microscopic probes were essentially nonexistent. We have studied pentamethylbenzene both above and below this transition using ^{13}C powder lineshapes. As may be seen from Fig. 1, above 24° the powder pattern is narrowed from the rigid molecule powder pattern, obtained below the transition. In these spectra the σ_{33} tensor element, which corresponds to a direction perpendicular to the plane of the molecule, is unchanged. This indicates that the narrowing must be caused by a motion in the plane of the molecule, which then averages σ_{11} and σ_{22} , the elements along the methyl group and orthogonal to it in the plane. The narrowing is consistent with a very rapid jumping of the molecules between two positions 40° apart, or a continuous torsional motion through some larger angle. Which of these actually takes place is an interesting question. Thus we predict that the phase transition is between ordered static molecules and partially mobile ones. The crystallographic packing which gives rise to this different molecular behavior and the exact nature of the motion are under investigation.

3. PROTON SPIN FLUCTUATIONS IN ORGANIC SOLIDS

M. Mehring and A. Pines

The notion of motional narrowing in NMR is a well-known one. In solids where molecules are rigid, broad spectroscopic lines are observed due to spin-spin interactions. As the temperature is raised, motion sets in causing a modulation and averaging of the interactions and yielding narrow lines. An analogous phenomenon can take place entirely in spin space. Consider an organic solid containing proton (^1H) and carbon (^{13}C , ~1% abundance) nuclei. The only mechanism for broadening of the ^{13}C resonance is the ^{13}C - ^1H spin couplings since the ^{13}C spins are naturally dilute. However, the ^1H - ^1H spin interactions can cause a modulation of the ^{13}C - ^1H coupling inducing motional narrowing. Quantum mechanically comes about because the H-H and C-H Hamiltonians do not commute:

$$[\mathcal{H}_{\text{HH}}, \mathcal{H}_{\text{CH}}] \neq 0$$

whereas $\mathcal{H}_{\text{HH}}$ and the C magnetization operator do:

$$[\mathcal{H}_{\text{HH}}, I_{\text{C}}] = 0.$$

The nature of the proton spin fluctuations is important and can be studied by observing the carbon lineshapes. In particular, if the proton couplings can be changed by radiofrequency experiments, the time correlations of the ^{13}C - ^1H modulation should change and so should the ^{13}C lineshape. We should be able to monitor thus directly the correlation function

$$Q(t) = \langle e^{-i\mathcal{H}_{\text{HH}}t} \mathcal{H}_{\text{CH}} e^{i\mathcal{H}_{\text{HH}}t} \mathcal{H}_{\text{CH}} \rangle$$

where $\mathcal{H}_{\text{HH}}$ is modified by the experiment. We have performed such experiments on solid polycrystalline adamantane, showing effects similar to our previous work on AgF. Figure 1 shows the broadening of the ^{13}C line when the ^1H - ^1H couplings are quenched eliminating the spin motional narrowing. Complete agreement with a quantitative theory is obtained. Using such experiments we are studying in detail the quantum mechanical spin fluctuations.

Fig. 1. Linewidths of the ^{13}C NMR signal in solid adamantane vs. the angle β of the effective field in the rotating frame of the protons. The ^1H - ^1H couplings transform as $P_2(\cos \beta)$ and thus approach zero at $\beta \sim 54.7^\circ$. The smooth lines are from various theoretical calculations, the top taking the ^1H - ^1H couplings into account and the lower one ignoring them. (XBL 756-1543)

4. OPERATOR FORMALISM FOR DOUBLE QUANTUM NMR*

S. Vega and A. Pines

We have developed a quantum mechanical operator formalism which describes the interaction of a spin-1 nucleus with a weak radiofrequency field. The Hamiltonian in the rotating frame is:

$$\mathcal{H} = -\delta\omega I_z - \omega_1 I_x + \frac{1}{3} \omega_Q (3I_z^2 - I^2)$$

where $\delta\omega$ is the resonance offset, ω_1 is the intensity of the rf field and $2\omega_Q$ is the quadrupolar splitting. Nine fictitious spin-1/2 operators, $I_{p,j}$ (where $p=x,y,z$ and $j=1,2,3$) are defined, which are the generators of the group $\text{SU}(3)$ and satisfy angular momentum commutation relations:

$$[I_{p,j}, I_{p,k}] = i I_{p,\ell}$$

where $j, k, \ell = 1, 2, 3$ or cyclic permutation. Thus each p defines a three-dimensional space termed p -space. For irradiation near the center of the I-spectrum, double quantum transitions ($m=1$ to -1) are induced and the formalism allows us to write the effective operators for these transitions. For example, if we take $\delta\omega, \omega_1 \ll \omega_Q$, we find the effective Double Quantum (DQ) Hamiltonian:

$$\mathcal{H}_{DQ} \approx -2\delta\omega I_{z,1} - \frac{\omega_1^2}{\omega_Q} I_{z,3}.$$

Thus the z -space is referred to as the DQ frame; it has effective magnetogyric ratio 2γ along the $z1$ (resonance offset) axis and $\omega_1/\omega_Q \gamma$ along the $z3$ (rf field) axis. Figure 1 depicts this situation schematically. Thus the DQ behavior is reduced to the study of rotations in this

Fig. 1. Double quantum rotating frame. If a spin-1 nucleus with quadrupolar splitting $2\omega_Q$ is irradiated near resonance ($\delta\omega$) with an rf field ω_1 such that $\omega_1 \ll \omega_Q$ double quantum transitions are induced. The effective Hamiltonian is

$$\mathcal{H}_{DQ} \approx -2\delta\omega I_{z,1} - \frac{\omega_1^2}{\omega_Q} I_{z,3}$$

and is depicted schematically in the figure.

(XBL 768-10220)

effective frame. This has provided a powerful formalistic basis for describing a variety of novel experiments performed in our laboratory: DQ coherence, DQ spin locking, Fourier transform DQ NMR, DQ spin decoupling, DQ double resonance, etc. The formalism is equally useful in describing two-photon phenomena in other regions of the electromagnetic spectrum, e.g., coherent two photon laser experiments.

Abstracted from LBL-5742.

5. FOURIER TRANSFORM DOUBLE QUANTUM NMR

S. Vega, D. E. Wemmer and A. Pines

We have measured the first high resolution NMR spectra of deuterium in solids. This allows the labeling of large molecules to study the local structure and dynamics, normally inaccessible by classical NMR. Figure 1 demonstrates that the

Fig. 1. Deuterium spin-1 energy levels are shifted by $-1/3 \omega_Q$ and $+2/3 \omega_Q$ due to interaction of the electric quadrupole with an axially symmetric electric field gradient. The transition $m = 1 \rightarrow -1$ is induced by a double-quantum transition at the unshifted frequency ω_0 , with a radiofrequency field of intensity $\omega_1 \ll \omega_Q$. (XBL 763-629)

deuterium spin-1 levels are shifted by quadrupolar interactions in such a way that extremely broad (~ 200 kHz) spectra are normally found. However, by a double quantum transition at ω_0 we can induce transitions between $m = \pm 1$. The coherent state thus produced oscillates at frequencies (2ω) independent of the quadrupolar splitting, i.e., the time dependent density operator is given by:

$$\rho(t) = I_{z,2} \cos 2\omega t - I_{z,3} \sin 2\omega t$$

where $I_{z,i}$ are coherent double quantum operators. By Fourier transformation of this time evolution, detected by a suitable train of pulses, a high resolution spectrum is obtained with resolution as good as 20 Hz, i.e., an improvement in resolution of 1000.

Figure 2 shows such a Fourier transform double quantum spectrum of the deuterium spins in solid polycrystalline benzene- d_1 . This is a good example since attempts at high resolution proton NMR in benzene have not been successful. The spectrum shows a powder pattern corresponding to the superposition of different resonance frequencies (chemical shift, σ) for different orientations of the benzene molecule. The diamagnetic shielding is higher when the magnetic field is in the plane of the molecule than when it is perpendicular to the plane. Other systems have been studied using this approach giving us an idea of anisotropic electronic currents in the molecules.

Fig. 2. Fourier transform double quantum NMR spectrum of deuterium in solid benzene- d_1 at -48°C doped 10% into normal benzene. One ppm in σ corresponds to 28 Hz. (XBL 764-1092)

6. DOUBLE QUANTUM SPIN LOCKING

S. Vega and A. Pines

In normal single quantum pulsed NMR, a system of spins aligned along the z-axis is irradiated

with a resonant $\pi/2$ pulse producing a coherent state by bringing the spin alignment away from the z-axis into the x-y plane. The coherent state is a macroscopic magnetic dipole (magnetization) that precesses about the z axis at frequency ω_0 inducing a voltage in a radiofrequency coil. The magnetization decays as the phases between spins become random. A very important technique for enhancing the lifetime of the magnetization by preserving phase coherence during the precession is spin-locking. This is done by phase shifting the rf field by $\pi/2$ following the preparation pulse. The magnetization is then aligned with the rf field and cannot decay due to conservation of spin energy if spin-lattice coupling is weak.

We have introduced and made practical the concept of double quantum spin locking. Following a $\pi/2$ double quantum pulse, a coherent electric quadrupolar state in the x-y plane is produced that precesses at $2\omega_0$. The symmetry of the quadrupolar components $I_{z,2}$ and $I_{z,3}$ is shown in Fig. 1 demonstrating a) why the precession is at

Fig. 1. Symmetry of the two coherent double quantum states $I_{z,2}$ and $I_{z,3}$. A $\pi/4$ phase shift takes $I_{z,2}$ into $I_{z,3}$ and can produce spin locking. A $\pi/2$ phase shift takes $I_{z,3}$ to $-I_{z,3}$ unlike the case of single quantum spectroscopy. (XBL 7610-4973)

$2\omega_0$ (the state returns to itself every π radians), b) that there is no observable signal induced in an rf coil (there is no macroscopic magnetic dipole), and c) the phase can be reversed producing spin echoes by a $\pi/2$ phase shift. Further, it can be seen from the symmetry that a $\pi/4$ phase shift is required to effect spin

locking of the double quantum quadrupolar state and to preserve the coherent phases and lifetime.

Figure 2 demonstrates an example of the double quantum spin locking with a $\pi/4$ phase shift on the

Fig. 2. (a) Double quantum free induction decay after a 90° double quantum pulse

$$\frac{\omega_1^2}{\omega_Q} t = \frac{\pi}{2}$$

on the carboxyl deuterons of crystalline oxalic acid dihydrate. The experimental points are compared with the theoretical line from our formalism. (b) The 45° phase shifted rf is expected to induce double quantum spin locking and indeed the resonance offset oscillation is removed and the decay prolonged substantially. (XBL 768-10206, -10207A)

deuterium spins of crystalline oxalic acid dihydrate. The lifetime of the coherent state is

indeed lengthened by an order of magnitude over normal free precession.

* Abstracted from LBL-5481, "Theory of Double-Quantum Coherence and High Resolution Deuterium NMR in Solids," presented at the XIXth Congress Ampere, Heidelberg, 1976.

7. AROMATIC/ALIPHATIC CARBON RATIO AND POLYCONDENSATION IN WHOLE AND PROCESSED COALS

D. E. Wemmer, L. Brodsky and A. Pines

Together with the Central Research Division of Mobil Oil Company and with EPRI and ERDA support, we are characterizing materials used in fuel technology, in particular coal and oil shale. Using solid state NMR techniques we can distinguish four types of carbon functional groups -- condensed aromatic, simple aromatic, oxygen bonded aliphatic, and simple aliphatic. This has been used to characterize coals by rank and to understand the changes that occur during processing of the coals. No large scale aromatic condensation is found in coals other than anthracite. The aromatic aliphatic ratio is found to be sensitive to contact time in liquification and an extensive table of characteristic data has been produced.

Figure 1 shows an example of spectra from two natural coal samples obtained directly in the solid state. The upper (Monterey) shows a much larger aromatic carbon content than the lower (Wyodack). Oxygen content, ether groups, and polycondensation have also been studied.

Fig. 1. Carbon-13 NMR spectra of solid coal samples. Upper curve, Monterey coal; lower curve, Wyodack coal. (XBL 773-430)

8. NUCLEAR SPIN EFFECTS IN CHEMICAL REACTIONS

L. Sterna, S. Bustamente and A. Pines

The Radical Pair Theory of Chemically Induced Dynamic Nuclear Polarization postulates that the yields of products derived from free radical reactions can exhibit a dependence upon nuclear spin state configurations in the free radicals. This dependence is caused by interaction of the nuclear and electron spins and is borne out by selective population of various nuclear spin states in the free radical products.

If such a mechanism is correct, it should also be possible to observe a dependence of the product yield upon the presence of isotopes of differing nuclear spin.

We have investigated two systems where we expect this nuclear "spin isotope effect" to be perceptible. The basic reaction scheme involves the photochemical formation of a radical pair and then the subsequent recombination of the two radicals. We have studied the probability of pair recombination as a function of ^{12}C (spin=0) vs. ^{13}C (spin=1/2) substitution within one of the partners of the radical pair.

The reaction is outlined in the following three steps:

- I. $M \xrightarrow{h\nu} M^*$ (Triplet excited state)
- II. $M^* + R-H \rightarrow M(H) \cdots R$ Radical Pair Formation
- III. $M(H) \cdots R \rightarrow M(H)-R$ Pair Recombination.

Mass spectral data for the two systems are summarized in the following table where the relevant experimental parameter is the ratio of recombination probability for pairs containing ^{13}C to pairs containing ^{12}C . An isotope effect is indeed observed.

M	R-H	$^{13}\text{C}/^{12}\text{C}$ Recombination Ratio
Diphenyldiazomethane	Toluene	1.05 ± 0.017
Benzophenone	Toluene	1.02 ± 0.017

Present research is centered around the detection of nuclear spin effects and, more generally, magnetic field effects on chemical reactions with emphasis on NMR and chemical techniques as a probe for investigating the physics of these processes. Extension to other pairs of isotopes is planned.

9. SYNTHESIS OF ISOTOPICALLY LABELED LIQUID CRYSTALS

H. Zimmermann and A. Pines

By labeling liquid crystal molecules with stable isotopes it is possible to enhance particular NMR signals, remove unwanted couplings by isotopic dilution, and assign otherwise unresolved resonances. Labeling with ^{13}C and deuterium has been accomplished with a variety of techniques and molecules.

Saturated aliphatic hydrocarbon chains have been labeled with controlled percentage of deuterium for use as components of lyotropic phases and as intermediates in the synthesis of chain deuterated thermotropic liquid crystals. Random deuteration to a desired percentage has been achieved by catalytic exchange of alkanolic acids with platinum oxide in an appropriate mixture of D_2O and H_2O . A mass spectrum of such a labeled sample of decanoic acid is shown in Fig. 1.

Fig. 1. Mass spectrum of ~10% deuterated decanoic acid used for incorporation into labeled liquid crystals. (XBL 7611-9876)

Partially deuterated alkoxyazoxybenzenes (I) have been prepared. The 2,6 dideutero-p-nitrophenol intermediate was synthesized by exchange of perdeuteroaniline with H_2O under pressure followed by nitration and diazotization.

I

TBBA is of particular interest because of its many mesomorphic phases. The high smectic transition temperatures make natural abundance ^{13}C -spectroscopy difficult. Therefore, a sample II enriched in the aldehydic positions was prepared by pyrolytic transcarboxylation of potassium- ^{13}C -benzoate with CdI_2 , to give the double labeled terephthalic acid that was esterified, reduced to the alcohol, and oxidized to the terephthalaldehyde.

Similarly, an analog, deuterated at the aldehydic positions, was prepared by reduction of terephthalic acid dimethylester with LiAlD_4 and oxidation of the alcohol with concentrated HNO_3 .

Several homologous series of compounds having mesomorphic phases at ambient temperatures and a variety of low temperature smectic phases have been prepared with specific deuteration of the chains and/or aldehydic positions. These include alkyl-cyanobiphenyls, alkoxy-cyanobiphenyls, and 4-alkoxy-benzylidene-4-alkylanilines. Chain lengths were varied between five and ten carbons.

In order to prepare single crystals of organic compounds for NMR investigations a continuous operation zone refiner and Bridgman type crystal growing apparatus have been constructed.

10. MOLECULAR CONFORMATION IN THE NEMATIC-SMECTIC TRANSITIONS

A. Höhener and A. Pines

Liquid crystals are composed of long rod-like molecules. They exist in a number of orientationally ordered phases, of which some of the common high temperature forms are shown in Fig. 1. The

Fig. 1. Some of the higher temperature liquid crystal phases. (XBL 748-7063)

study of these materials is important since they serve as displays, models for phase transitions and biological membranes, orienting environments for stereochemistry, etc. An important, to date largely unanswered question, is what properties of the molecular conformation cause condensation into the different phases. We have studied the nematic and smectic-A phases of a series of liquid crystals deriving from cinnamic acid and p-ethoxy benzaldehyde, to see whether the phase transition correlates with any molecular property.

Figure 2 shows an example of the ^{13}C NMR line positions vs. temperature for one such compound.

Fig. 2. Dependence of the ^{13}C NMR frequency on temperature in a liquid crystal with a nematic-smectic-A phase transition. Each line represents one carbon position from which the conformation of the molecule can be studied. (XBL 7611-9868)

From the change in frequency (vertical scale) at the nematic-smectic transition, we can measure the order parameter and further, we infer that a change in molecular conformation takes place. This is depicted schematically in Fig. 3; in the

nematic phase the end chain appears to be free relative to the aromatic core, whereas in the smectic phase its mobility appears to be impaired. Such molecular properties and the degree to which they drive the phase transitions are teaching us about the nature of liquid crystalline behavior.

Fig. 3. Conformational change in liquid crystal molecule. The ellipse designates the aromatic core. At left is the high temperature conformation with the end chain moving freely in a cone. At right, below the phase transition the chain becomes immobile. (XBL 7611-9870)

11. MOLECULAR ORIENTATIONAL ORDER IN NEMATIC LIQUID CRYSTALS

A. Höhener and A. Pines

We have continued our investigation of the molecular order in liquid crystal phases. Consider a fluctuating molecule with orientation $\Omega(t) \equiv (\alpha, \beta, \gamma)$ relative to a magnetic field, where β is the angle between the long axis of the molecule and the field and γ is the angle about the long axis. The spin Hamiltonian is given by:

$$\mathcal{H}(t) = \sum_m F_{2m}(t) T_{2-m} \quad (1)$$

where $F_{2m}(t)$ are spatial operators dependent on the orientation of the molecule and T_{2-m} are spin operators. This can be written

$$\mathcal{H}(t) = \sum_{m'm} D_{m'm}^{(2)}(\Omega) F_{2m'} T_{2-m} \quad (2)$$

where $F_{2m'}$ are now fixed in the molecular axes. $D_{m'm}^{(2)}$ are Wigner transformation matrix elements from the molecular to magnetic field axes and are time dependent through Ω . If the fluctuations are rapid, then we perform an average:

$$\mathcal{H} = \sum_{m'm} \langle D_{m'm}^{(2)}(\Omega) \rangle F_{2m'} T_{2-m} \quad (3)$$

The objects $\langle D_{m'm}^{(2)}(\Omega) \rangle$ appearing in (3) are called order parameters and are important in understanding the molecular statistical behavior of these phases. Two of the order parameters we

have measured in a series of nematic liquid crystals are:

$$S \equiv \langle D_{00}^{(2)} \rangle = \left\langle \frac{1}{2} (3 \cos^2 \beta - 1) \right\rangle$$

$$D \equiv \langle D_{0\pm 2}^{(2)} \rangle = \langle \sin^2 \beta \cos 2\gamma \rangle$$

S measures to what degree the long axes are aligned whereas D measures the anisotropy of motion about the long axes (or the anisotropy in fluctuation of the long axis.) Figure 1 shows

Order Parameters

$$P = \langle \cos \theta \rangle$$

$$S = \left\langle \frac{1}{2} (3 \cos^2 \theta - 1) \right\rangle$$

Fig. 1. Analogy of isotropic-nematic and paramagnetic-ferromagnetic transitions. S measures the orientational order of the long molecular axis in the nematic phase. The transitions follow Landau de Gennes theory qualitatively. (XBL 764-1276)

the nature of the nematic ordering in analogy to ferromagnetism. The following table compares measurements of our microscopic order parameter S with macroscopic laser birefringence measurements of Shen et al. in a homologous series of nematics (n = number of carbons on end chain) at 5°C below the phase transition.

n	1	2	3	4	5	6	7	8	9
S (NMR)	0.525	0.577	0.546	0.596	0.562	0.590	0.603	0.666	0.725
S (optical)	0.493	0.577	0.550	0.580	0.562	0.583	0.604	--	--

The optical measurements are not absolute and have been normalized to ours at $n=2$. These data agree qualitatively with the Landau de Gennes theory of the isotropic-nematic transition and correlate with the square root of the transition entropy except in higher analogs ($n \geq 7$) where low lying smectic phases exist. We find also for the first time values of D for the nematic phase. These range from 0.00 to 0.05 with temperature, showing that the single order parameter approximation is invalid.

12. PHASE TRANSITIONS AND ORDER IN P-PENTOXYBENZYLIDENE-p-HEPTYLOXYANILINE

A. Höhener, B. Bicknell and A. Pines

A singly deuterium labeled analog of p-pentoxybenzylidene-p-heptyloxyaniline (50.7) has been prepared. This compound is of particular interest since it displays viscous low temperature smectic-B phases. The deuterium NMR spectrum is dominated by the quadrupole interaction and gives a direct picture of the degree of molecular orientational order. Figure 1 shows such a sharp

Fig. 1. Deuterium NMR spectrum of deuterium labeled (50.7) showing quadrupolar splitting due to molecular orientational order. (XBL 7611-9869)

quadrupole split spectrum in the smectic-A phase. By following the splitting vs. temperature it should be possible to study the phase transitions of this material. Indeed, Fig. 2 shows the richness of phases observed by our NMR spectra in agreement with thermodynamic and x-ray data.

We see that the smectic-A to smectic-C transition is second order, whereas the smectic-C to smectic-B_A transition is strongly first order. It is very surprising that the molecules appear to have a tilted phase (molecular axes tilted away from the normal to the molecular planes) in the smectic-C phase between two untilted phases (smectic-A and B_A) in which the molecular axes are perpendicular to the planes. The nature of the orientational order and molecular conformation in these low temperature phases is under study.

Fig. 2. Temperature dependence of quadrupolar splitting in (50.7). The first order phase transitions are accompanied by a finite change in splitting and the second order ones by a change of slope. (XBL 7611-9874)

13. ANALYSIS OF CHAIN ORDERING BY NMR

D. Weitekamp and A. Pines

The measurement of the motionally averaged quadrupole and direct dipole-dipole interactions in NMR has been extensively exploited as a structural tool in the study of liquid crystals. The hydrocarbon chain region of liquid crystal molecules poses a particularly difficult problem, because of the overlapping of resonances from different nuclei and the many possible configurations which the chain can take by rotational isomerization about the carbon-carbon single bonds (Fig. 1).

Fig. 1. Projection diagram of possible rotamers at a carbon-carbon single bond in a chain. (XBL 771-7397)

We have developed a theoretical analysis which relates all possible measurements of motionally averaged anisotropic NMR interactions to a minimum number of unknowns describing the rotational isomerization and the ordering of the rotamers. This analysis provides stringent experimental tests of models of chain ordering by relating to experimental observables such as physically interesting quantities as configurational probabilities, correlations between configurations at nearby bonds, and order parameters. The analysis shows that knowledge of averaged deuterium quadrupole couplings alone at each chain segment is not sufficient to test predictions of these quantities.

Multiple resonance experiments designed to measure the necessary interactions are in progress on isotopically labeled thermotropic and lyotropic liquid crystals. Application to biological systems is foreseen.

14. RESEARCH PLANS FOR CALENDAR YEAR 1977

Alexander Pines

1. Extend the nuclear magnetic isotope effect to other photochemical reactions and to other pairs of isotopes.
2. Study the relationship between molecular properties and the behavior of liquid crystal phases and phase transitions.
3. Continue the development of our NMR technique of Fourier Transform Double Quantum Spectroscopy. Extend to allow us to obtain isotropic spectra and to other quadrupolar nuclei (e.g., ^{14}N).
4. Apply our techniques to several practical problems including molecules adsorbed on surfaces, fuel processing and quantum mechanical tunneling in solids.
5. Begin a new project on the study of molecular properties in crystals by NMR in excited states.
6. Study the statistical mechanics of interacting aliphatic chains in lyotropic phases. Continue the synthesis of specifically deuterium labeled chemicals where required for this project.

15. 1976 PUBLICATIONS AND REPORTS

Alexander Pines and Associates

Journals

1. M. Mehring and G. Sinning, NMR Line-Broadening in Solids by Slowing Down of Spin Fluctuations, Z. Phys. 24, 73 (1976).

2. D. J. Ruben, S. Vega and M. Mehring, New Approach to High Resolution Proton NMR in Solids: Deuterium Spin-Decoupling by Multiple-Quantum Transitions, Phys. Rev. Lett. 36, 110 (1976).

3. D. E. Wemmer, Application of Novel NMR Techniques to Coal Structure, Proceedings of the Coal Chemistry Workshop, Stanford, p. 229 (1976).

4. G. Sinning and M. Mehring, Dynamics of Spin Decoupling in Carbon-13-Proton NMR, Chemical Physics Lett. 43, 382 (1976).

5. S. Vega and T. W. Shattuck, Fourier Transform Double-Quantum NMR in Solids, Phys. Rev. Lett. 37, 43 (1976).

Invited Lectures

1. Dynamical Symmetry and NMR Lineshapes in Solids, 17th Experimental NMR Conference, Pittsburgh, April, 1976, LBL-4935.

2. Multiple-Quantum NMR in Oriented Phases, 17th Experimental NMR Conference, Pittsburgh, April, 1976, LBL-4936.

3. Fourier Transform Double Quantum NMR, NMR Symposium of the 7th Northeast ACS Meeting, Albany, August, 1976, LBL-5133.

4. Multiple Quantum NMR, International Summer School on Magnetic Resonance and Phase Transitions, Pula, Yugoslavia, September, 1976. Three lectures.

5. New Developments in NMR--Are Many Photons Better Than One?, FACSS Joint Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, November 1976, LBL-5468.

6. Coal Group, Chemical Engineering Department, University of California, Berkeley, February 1976.

7. Chemistry Department, University of California, Los Angeles, March, 1976.

8. Chemistry Department, San Francisco State University, March, 1976.

9. Central Research Division, Mobil Research and Development Corporation, Princeton, April, 1976.

10. Physics Department, University of Dortmund, West Germany, September, 1976.

11. Physics Department, University of Delft, Holland, September, 1976.

12. Chemistry Department, Columbia University, New York, November 1976.

Presentations and LBL Reports

1. T. W. Shattuck, Pulsed Nuclear Magnetic Double Resonance Spectrometer, LBL-5781.

2. D. Wemmer and S. Vega, Double Quantum NMR in Powders, presented at the 17th Experimental NMR Conference, Pittsburgh, Pennsylvania, April, 1976, LBL-4976 Abs.
3. A. Höhener, Carbon ^{13}C Tensors from Complex Powder Spectra and Application to Liquid Crystals, presented at the 17th Experimental NMR Conference, Pittsburgh, Pennsylvania, April, 1976, LBL-4946 Abs.
4. S. Vega, Theory of Double Quantum Coherence and High Resolution Deuterium NMR in Solids, Proceedings of the 19th Ampere Congress, Heidelberg, 1976, LBL-5481.
5. S. Vega, Operator Formalism for Double Quantum NMR in Solids, LBL-5742.
6. S. Allison, Carbon-13 NMR Studies of Liquid Crystal Systems, (M.S. Thesis), LBL-4506, 1976.
7. T. W. Shattuck, Carbon and Deuterium Nuclear Magnetic Resonance in Solids, (Ph.D. Thesis), LBL-5458, 1976.
8. D. J. Ruben and D. E. Wemmer, Dynamical Symmetry and NMR Lineshapes in Solids, 19th Ampere Congress, Heidelberg, September, 1976, LBL-5160.

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II.

Molecular Sciences

A. RADIATION AND SEPARATION RESEARCH

1. RADIATION SCIENCES

a. Photochemistry of Materials in the Stratosphere

Harold S. Johnston, Principal Investigator

(I) Experimental Studies

1. DEVELOPMENT OF HIGH-INTENSITY, LASER-FLASH PHOTOLYSIS METHOD FOR STUDY OF PHOTOCHEMICAL REACTIONS*

Frank Magnotta, John Girman, and David Littlejohn

Historically, conventional flash photolysis provided kineticists and spectroscopists with a rudimentary but viable method for investigation of short-lived (intermediate) species. However, long flashes of broad band radiation, low flash rates, unwanted infrared heating, and difficult to use detection systems have limited its widespread applicability.

We have developed an evolutionary improvement in this technique by replacing flash lamps with a high power tunable laser and implementing a significantly improved detection system. Some of the benefits derived from utilizing a tunable dye laser include the following:

- Wavelength dependent photolytic source, with continuous narrow band width tunability from the far UV to near IR.
- Spectral Condensation -- the ability to channel high optical power into a small oscillating band width without loss of significant energy (i.e., high optical purity at high power).
- No direct infrared heating from the flash source.
- Shorter ($< 1 \mu\text{sec}$) pulse widths (which can be further shortened electro-optically or made ultrashort by mode locking) to facilitate investigation of short-lived intermediates, obviating deconvolution of flash and signal.
- Relatively high pulse repetition rates useful for signal accumulation and averaging.
- High spatial coherence allowing the laser to be physically removed from the detection system, thus reducing rf pickup.
- Ability to completely photolyze molecules with moderate to high absorption cross sections, which both produces a known concentration of primary products and simultaneously eliminates the possibility of secondary reactions between reactants and products, simplifying subsequent kinetic interpretation.

Our data acquisition system consists of a modular vacuum chamber to allow several modes of detection; the method of choice for the current series of experiments being atomic and molecular resonance fluorescence in the vacuum ultraviolet. This detection technique is both highly specific and extremely sensitive, allowing utilization of very small initial concentrations of reaction, which keeps the system optically thin and the percentage of laser radiation absorbed very small. This further reduces the probability of significant heating due to absorption, while still allowing high degrees of photolysis. The use of small concentrations in these systems and their subsequently low fluorescence scattering intensities necessitates photon counting techniques rather than conventional dc detection.

This high level digital-signal processing is, by nature, immune to noise pickup as photon counts are sent to a fast digital multichannel analyzer for final-signal accumulation and interpretation by a dedicated laboratory computer. Data reduction and analysis is further aided by our ability to simulate the kinetic system in question (with the larger LBL 7600 computer) using numerical rate integration techniques.

*Supported in part by the National Science Foundation.

2. USING MOLECULAR BEAMS TO STUDY ATMOSPHERIC REACTIONS

Marta Kowalczyk (in collaboration with Y. T. Lee)

The probing of the reaction mechanism has been extended to shorter and shorter time scales, thereby hoping to capture information about the primary chemical event. Kineticists who work in the bulk phase usually accept the fact that their work is often complicated by secondary reactions among the free radical products and by wall reactions. At extremely short time scales low concentrations of products and lack of appropriate monitoring devices becomes more troublesome. The result of such difficulties is that in some cases primary reaction products have not been yet identified and in other cases large uncertainties exist in the measured rate constants. In general, bulk techniques are not suitable for obtaining details about the collision dynamics and microscopic information such as the intermolecular potential because the multiple collisions average the quantities one wishes to measure.

One approach to studying reactions difficult to handle in bulk experiments is by using molecular beam scattering. The single collision time scale removes the inherent averaging and difficulties due to subsequent reactions in a bulk system. From a molecular beam experiment one obtains information about reaction dynamics by measuring the differential cross section or angular distribution pattern which is directly determined by the potential energy hypersurface. Dynamical information such as the molecular geometry of the collision, the duration of the collision, and whether the collision went by a direct mechanism or through a complex intermediate can be obtained. The integration of the differential cross sections gives the total cross section and a study of the velocity dependence can give the activation energy of the reaction. Product velocity measurements give information about energy disposal in the reaction. The presence of elastic scattering allows one to fit the scattering data to an intermolecular potential. The presence of simultaneous elastic and reactive channels also allows one to normalize the reactive cross section since the elastic cross section can be related to a calculated value in the long range interaction region.

A joint project of this laboratory and that of Y. T. Lee has been directed to the goal of obtaining the total cross section as a function of velocity for the reactions $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$ and $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$, both atmospheric reactions well-characterized by bulk kinetic experiments. The data will also give information about the reaction dynamics which can be used in subsequent calculations. Although in principle one can obtain bulk macroscopic properties, such as the rate constant from microscopic data and such as the total cross section by massive averaging, difficulties in obtaining absolute values for the total cross section, and difficulties in preparing reactants in various internal energy states make this approach too imprecise for good values of the rate constant.

Preliminary scattering experiments have been done for the $\text{O}_3 + \text{Cl}$ reaction. The Cl beam was prepared by thermal dissociation and seeded in various carriers. O_3 was prepared by silent electric discharge of O_2 , stored at dry ice temperatures on silica gel and desorbed with the desired carrier. Both source gases were supersonically expanded through a nozzle which results in a narrow energy spread ideally suitable to velocity dependence studies. Further experiments on this system are in progress. The $\text{NO} + \text{O}_3$ reaction can be studied in two ways, that is, by scattering and by the chemiluminescence of the excited NO_2 product. Studies of the velocity dependence of the chemiluminescence are planned for the near future.

3. IMPROVED MOLECULAR MODULATION SPECTROMETER FOR THE STUDY OF HOO RADICAL REACTIONS

James Podolske

Although the technique of molecular modulation

spectroscopy has been in existence for several years in various forms, its use has been limited. Since the techniques of frequency domain kinetics are not nearly as well-known or developed as techniques of time domain kinetics, many improvements on the older versions of molecular modulation are possible. The spectrometer we are currently constructing promises to be the most sensitive instrument of its type yet constructed.

The apparatus consists of a dual beam optical train, a 1-3/4 meter quartz reactor vessel, a monochromator, detectors, and associated electronics. Reactants are flowed into the quartz reactor through glass dispersion tubes, then undergo irradiation by UV light from mercury resonance lamps, which run the length of the vessel and undergo some photochemistry. The vessel is set up as a multipath White cell, with pathlength adjustable from 7.5 to 30 meters, to monitor the absorption of the chemical species present. The entire cell is surrounded by an insulated box so that reactions can be run from -40°C to $+50^\circ\text{C}$. Finally, the whole apparatus is mounted on a vibration damped table to isolate it from building vibration.

The technique of molecular modulation spectroscopy involves perturbing a steady-state photochemical system by modulating the light intensity in some manner, looking at the phase and the amplitude of the fluctuations in concentration of reactants, intermediates and products caused by the perturbations, and then inferring chemical kinetic parameters for them. In the past this perturbation took the form of square wave "on-off" modulation. This can lead to such severe perturbation of the system that interpretation of the results requires fitting to computer kinetics models, as the steady-state conditions are not good first order approximations to the actual conditions throughout the cycle. In our new instrument the light will be modulated sinusoidally about a reference level so that the modulation is at all times a relatively small perturbation on the steady state. This makes interpretation of the experimental results much simpler, as most cases will then be well described by simple analytical equations. Another advantage of sine wave modulation is that only the fundamental frequency is excited, so that one doesn't have to worry about interference of higher harmonics in the phase sensitive detection system.

Other improvements made in this instrument over previous ones are the dual beam detector system and increased photolysis light intensity. The optical train consists of two beams, one which gets chopped at 1.8 kHz, passes through the cell and then to the monochromator, and another which is just chopped at 1.02 kHz and passes into the monochromator. The signal from the detector then passes into two lock-in analyzers, which were assembled in our laboratory; one extracts the reference signal at 1.0 kHz, the other the absorption signal at 1.8 kHz. These are then fed through a precision divider, and either digitized and sent to a PDP/8 computer or fed into an Ithaco lockin analyzer, which extracts the low frequency chemical modulation signal at the frequency of the

photolysis lamps. The use of aluminum mirrors and CaF_2 windows allows this instrument to operate in the spectral range from 0.2 - 9.5 μm . With this instrument we expect to be able to measure optical absorbances as low as 10^{-4} , and absorbance modulations as low as 10^{-6} .

4. ABSORPTION SPECTRUM OF NITROUS OXIDE AT LOW TEMPERATURES*

Gary Selwyn

Nitrous oxide is the major source of stratospheric nitric oxide and nitrogen dioxide. The temperature of the stratosphere varies from about 190 to 280 K. The absorption spectrum of nitrous oxide has been observed to vary with temperature above 300 K. This study is to evaluate quantitatively how the absorption spectrum varies at stratospheric temperatures. These data are needed for realistic calculations in the three-dimensional atmosphere of the rate of formation of nitric oxide from nitrous oxide.

*Supported in part by the National Science Foundation.

5. DEVELOPMENT OF GROUND-BASED METHOD TO MONITOR STRATOSPHERIC NITROGEN DIOXIDE*

Peter Connell and David Johnston

We have been developing a method for observing the vertical column and approximate vertical distribution of nitrogen dioxide in the stratosphere. The method collects visible light in a small telescope, both directly from the sun and scattered light from the zenith sky. Since we started this work, Noxon of the National Center for Atmospheric Studies¹ has developed a similar system and used it on a 12,000 foot high mountain peak and from aircraft. The aircraft have covered latitudes from Alaska to central South America. By now it is apparent that Noxon's work is far ahead of ours, and our work is being phased out.

*Supported in part by the National Science Foundation.

1. R. S. Hyde and J. F. Noxon, Stratospheric NO_2 Observations at Fritz Peak Observatory, Fall Annual Meeting of American Geophysical Union, San Francisco, Calif., Dec. 6-10, 1976.

(II) Theoretical Studies

6. ANALYSIS OF THE INDEPENDENT VARIABLES IN THE PERTURBATION OF STRATOSPHERIC OZONE BY NITROGEN FERTILIZERS*

Harold S. Johnston

For several years it has been apparent that

human fixation of nitrogen is approaching the natural rate of fixation of nitrogen,¹ and since 1972 several people have discussed the following chain of events: human fixation of nitrogen, denitrification to increase nitrous oxide, increased production of stratospheric nitric oxide, reduction of stratospheric ozone, etc. Only recently have there been attempts quantitatively to assess this sequence of events (summarized at a session of the AGU Meeting, Washington, D.C., April 1976). Different authors have found rather widely different values for the expected ozone reduction and for the time for it to appear. We have examined the essential independent variables in this problem and the uncertainties in them. There is at least a ten-fold uncertainty range in this problem, and much of the uncertainty concerns the biological aspects of the global nitrogen cycle. However, there is a coupling between the uncertainties such that a small ozone reduction is coupled to a relatively rapid onset and a large ozone reduction would occur only after a long time. The range is roughly as follows (for fertilizer use at the rate projected for year 2000):

Ozone reduction	Time of response
~ 2%	Decades
~ 20%	Centuries

*Supported in part by the National Science Foundation.

1. C. C. Delwiche, The Nitrogen Cycle, Scientific American 223, 137 (1970).

7. REVIEW OF LITERATURE STUDIES OF THE KINETICS OF HO AND HOO REACTIONS

Herbert Nelson

Some reactions of hydroxyl (HO) and perhydroxyl (HOO) radicals are important in the atmosphere and exceedingly difficult to measure in the laboratory. Some laboratory measurements involve complex systems and observed rate ratios, and the data are interpreted in terms of simplified sets of reactions. We have examined certain literature studies, have taken their initial conditions, and have calculated their observable quantities using a 40 or 50 reaction mechanism and our "Chem-constant" computer program based on the Gear routine. In this way we can see if reactions omitted by the authors had a significant effect on their observations. In some cases we confirmed the authors' analysis of their data, and in one case we found that there was a large systematic error in the estimated rate-constant ratios.

8. PHOTOCHEMISTRY IN THE STRATOSPHERE (A REVIEW)

Harold S. Johnston

The current understanding of stratospheric

photochemistry and dynamics is based partly on direct observations and partly on model calculations. At present it is desirable to increase the ratio of observations to calculations in this subject, although some components of the problem are now well-established.

Ozone is formed from far ultraviolet solar radiation and oxygen in the middle and upper stratosphere. The local and the global rates of ozone formation can be reliably evaluated. Of the ozone formed below 45 km, 20 to 30% is destroyed by ozone itself, 10 to 20% is destroyed by free radicals derived from water, and 50 to 70% is catalytically destroyed by natural stratospheric oxides of nitrogen. The natural rate of production of stratospheric nitrogen oxides is known, and this source strength provides a simple, general measure of how large man-made pollution of the stratosphere would have to be in order to cause a large reduction of ozone. Current civilian aircraft, current military aircraft, and the proposed 50 space shuttles per year add ozone-destroying catalysts to the stratosphere at a rate much less than their natural formation. A fleet of supersonic, passenger aircraft that would be large enough to pay for its development costs or continuous usage of chlorofluorocarbons at the current rate would each add ozone-destroying catalysts to the stratosphere at about the same rate that nature now produces stratospheric nitrogen oxides. To estimate the magnitude of ozone reduction caused by this approximately doubling of ozone-destroying catalysts, one must turn to the detailed model calculations involving two or three dimensions of atmospheric motions; such computations were quoted in this review.¹⁻⁸

1. The Natural Stratosphere of 1974, CIAP Monograph 1 (Department of Transportation. DOT-TST-75-51, National Technical Information Service, Springfield, Virginia 22151. Sept. 1975) 1350 pp.
2. The Stratosphere Perturbed by Propulsion Effluents, CIAP Monograph 3 (Department of Transportation. DOT-TST-75-53, National Technical Information Service, Springfield, Virginia 22151. Sept. 1975) 765 pp.
3. A. J. Grobecker, S. C. Coroniti, and R. H. Cannon, Jr., The Effects of Stratospheric Pollution by Aircraft, CIAP Report of Findings (Department of Transportation. DOT-TST-75-50, National Technical Information Service, Springfield, Virginia 22151. March 1975) 850 pp.
4. Environmental Impact of Stratospheric Flight (National Academy of Sciences - National Research Council, Washington, D.C. April 1975) 348 pp.
5. M. Nicolet, *Rev. Geophys. Space Phys.* **13**, 593 (1975).
6. F. S. Rowland and M. J. Molina, *Rev. Geophys. Space Phys.* **13**, 1 (1975).
7. H. S. Johnston, *Rev. Geophys. Space Phys.* **13**, 637 (1975).
8. T. Shimazaki and R. C. Whitten, *Rev. Geophys. Space Phys.* **14**, 1 (1976).

9. EXPECTED SHORT-TERM LOCAL EFFECT OF NUCLEAR BOMBS ON STRATOSPHERIC OZONE*

Harold S. Johnston

Nuclear bomb tests in the atmosphere produce both oxides of nitrogen and ozone. For bomb yields of 1 Mt or more, much of the bomb-produced radioactivity, ozone, and NO_x are lifted into the stratosphere. Bomb-produced NO_x constitutes a prompt one-time source of ozone if NO₂ is in excess of NO relative to the ambient NO₂/NO ratio, and it constitutes a fast (minutes) one-time destruction of ozone if NO is in excess. At a considerably slower, elevation-dependent rate, the bomb-produced NO_x is expected catalytically to destroy some stratospheric ozone. A 2 Mt nuclear bomb, exploded near 15°S on 4 July 1970, stabilized between 15 and 20 km with maximum concentration of radioactivity at 18 km. Christie¹ deduced the trajectory and size of this nuclear-bomb cloud for 10 days, and he examined the detailed record of total ozone observed at that time by the Nimbus 4 satellite. We have carried out calculations for several chemical processes expected to occur in this nuclear-bomb cloud. There is a wide range of uncertainty as to how much NO_x and ozone the nuclear bomb injected into the stratosphere. The central expectation value, referred to 18 km, is that bomb-produced ozone would increase the local concentration of stratospheric ozone by 40% on the first day; upon expansion of the cloud the increase drops to 2% by the eighth day; and it would require two months for the bomb-produced NO_x to destroy the bomb-produced ozone. There would be very little NO_x catalytic destruction of stratospheric ozone from this nuclear bomb during its first 10 days; it did not rise high enough into the stratosphere to cause a fast destruction of ozone. The observations by Christie are in agreement with current models of nuclear bombs and stratospheric photochemistry.

*Supported in part by the National Science Foundation.

1. J. Christie, *J. Geophys. Res.* **81**, 2581-2594 (1976).

10. USE OF THE SCIENTIFIC METHOD TO PREDICT COMPLEX FUTURE EVENTS

Harold S. Johnston

The recently concluded Climatic Impact Assessment Program (CIAP, 1972-1975) provides an interesting case history of the use of the scientific method to predict a complex, socially important, possible future event. The event is so complex that it cannot, as a whole, be taken into the laboratory for demonstration. The scientific methodology for such predictions is to break the problem down into "components" that

are observable, measurable, or otherwise capable of being analyzed. In this way experts in various fields work on their part of the complex problem. The overall process is factored into five stages: (1) The recognition of the opportunity or hazard is built on some components of the problem; (2) The identification of the larger set of components that, when evaluated, will give a meaningful representation of the future event constitutes the formulation of program to verify or disprove the contention of stage 1; (3) The evaluation of components set up in stage 2 is carried out in the straightforward manner by which the scientific method obtains, tests, and refines its data. During the course of evaluation, some components identified in stage 1 may be found to be unimportant or other components may be recognized and added to the set; (4) Using the scientific data obtained for all of the components, it is a straightforward scientific deduction to predict the future event, within the "universe of discourse" defined by stage (2). The scientific prediction based on component data is incomplete unless it includes the expectation value and the uncertainty range; (5) At the social or political level, policy decisions may be made whether to take steps to realize the predicted opportunity or to avoid the predicted hazard.

11. RESEARCH PLANS FOR CALENDAR YEAR 1977

Harold S. Johnston

With our new, high-intensity, flash laser, we plan to carry out several studies: (1) We plan to measure the production of $O(^1D)$ by flash photolysis of ozone with the tunable, doubled, dye laser, and detection of $O(^1D)$ from the light emission of singlet sigma molecular oxygen following $O(^1D)$ quenching ($O(^1D) + O_2 \rightarrow O + O_2(^1\Sigma)$). This study will cover the effects of wavelength and temperature; (2) In the lower stratosphere and in the troposphere the photolysis of the nitrate free radical NO_3 is an important ozone-destroying process if it occurs as $NO_3 \rightarrow NO + O_2$, but it is neutral with respect to ozone if it occurs as $NO_3 \rightarrow NO_2 + O$. Both processes occur (Graham, this laboratory, 1975) but the sum of the two quantum yields is less than one. By tunable laser flash photolysis of NO_3 , by resonance fluorescence detection of NO and of O, and by measuring the fluorescence of NO_3 , we plan to measure the absolute and relative quantum yields for NO_3 light absorption; (3) Similarly, by resonance fluorescence of the hydroxyl free radical, we plan to measure the wavelength dependent quantum yield for nitric acid photolysis.

By the infrared molecular-modulation method, we plan to study the photolysis of N_2O_5 with emphasis on absolute quantum yields and on primary products ($NO_2 + NO_3$, $N_2O_4 + O$, ...). With the new ultraviolet-visible molecular-modulation apparatus we plan to concentrate on measuring kinetics of the HOO free radical. In particular, we plan to measure rates of reaction for:

Also we will look for the spectra of the $HO_2:H_2O$ complex which has been previously postulated to exist.

In collaboration with Y. T. Lee we are exploring the possibility of using crossed molecular beams to measure or to infer rate constants for atmospheric reactions that can be satisfactorily measured in no other way. The first stage is to study known fast reactions ($Cl + O_3$, $NO + O_3$) by the molecular beam method, and then extend it to other cases that appear feasible.

We have two systems for the study of absorption spectra of atmospheric species at low temperatures. One is a Cary 118 spectrometer with a special long-path cell, and the other is the improved molecular modulation system. We will continue to measure the spectra of stable atmospheric species (N_2O , O_3 , O_2 , NO_2) as a function of pressure and temperature and to look for unusual species such as $HO_2:H_2O$ and $HOONO_2$.

12. 1976 PUBLICATIONS AND REPORTS

Harold S. Johnston and Associates

Journals and Articles

1. H. S. Johnston and E. Quitevis, The Oxides of Nitrogen with Respect to Urban Smog, Supersonic Transports, and Global Methane, Proceedings of the Fifth International Congress of Radiation Research, Seattle, Washington, July 14-20, 1974, O. F. Nygaard, H. I. Adler, W. K. Sinclair and M. J. Loops, Eds., Academic Press Inc., 1975.
2. G. E. Streit and H. S. Johnston, Reactions and Quenching of Vibrationally Excited Hydroxyl Radicals, J. of Chem. Phys. 64, 95 (1976) (LBL-3926).
3. H. S. Johnston, D. Kattenhorn and G. Whitten, Use of Excess Carbon 14 Data to Calibrate Models of Stratospheric Ozone Depletion by Supersonic Transports, J. of Geophys. Res. 81, 368 (1976) (LBL-3548).
4. H. S. Johnston, Photochemistry in the Stratosphere, Proceedings of the Loen Conference on Tunable Lasers and Applications, Norway, 1976, A. Mooradian, T. Jaeger, P. Stokseth, Eds., Springer-Verlag Berlin, 1976.

5. G. E. Streit, G. Z. Whitten, and H. S. Johnston, The Fate of Vibrationally Excited Hydroxyl Radicals, $\text{HO}(v \leq 9)$, in the Stratosphere, *Geophys. Res. Lett.* 3, 521 (1976) (LBL-5431).

Presented Papers

- A. National Sigma XI Lectureship by H. S. Johnston: "Pollution of the Stratosphere," Yale University, New Haven, Connecticut, February 23, 1976.
Olin Research Center, New Haven, Connecticut, February 24, 1976.
Indiana University of Pennsylvania, Indiana, Pennsylvania, February 24, 1976
Texas Technological College, Lubbock, Texas, March 31, 1976.
New Mexico State University, Las Cruces, New Mexico, April 1, 1976.
California State College, Bakersfield, California, May 3, 1976.
California State College, Northridge, California, May 5, 1976.
- B. Other Seminars: "Pollution of the Stratosphere" University of California, Davis, California, January 14, 1976.

Mechanical Engineering, University of California, Berkeley, California, January 21, 1976.
University of California, Santa Cruz, California, February 11, 1976.
Ripon College, Ripon Wisconsin, March 8-9, 1976.

- C. "Analysis of the Independent Variables in the Perturbation of Stratospheric Ozone by Nitrogen Fertilizers," Annual Meeting of American Geophysical Union, Washington, D.C., April 13-16, 1976.
- D. "Photochemistry in the Stratosphere," Loen Conference on Tunable Lasers and Applications, Loen, Norway, June 7-11, 1976.
- E. "Expected Short-Term Local Effect of Nuclear Bombs on Stratospheric Ozone," American Geophysical Union Meeting, San Francisco, California, December 6-10, 1976.
- F. "Use of the Scientific Method to Predict Complex Future Events," American Geophysical Union Meeting, San Francisco, California, December 6-10, 1976.

B. CHEMICAL AND GEOPHYSICAL ENERGY

1. CHEMICAL ENERGY

a. Formation of Oxyacids of Sulfur from SO₂

Robert E. Connick, Principal Investigator

1. THE CHEMISTRY OF SULFUR DIOXIDE SOLUTIONS

R. E. Connick and E. von Deuster

Sulfur dioxide is the most serious gaseous pollutant from stationary power plants. With the rising use of high-sulfur coal, effective and economical means of removing sulfur dioxide from stack gases assumes increasing importance. Present technology is generally based on aqueous scrubbing of the flue gas to absorb the sulfur dioxide. Since the chemistry of these processes is not thoroughly understood, the present work was undertaken to develop a more complete understanding of the basic chemistry of aqueous sulfur dioxide solutions, its ions formed by dissociation, its oxidation and reduction products, and the kinetics of interconversion of these species in such solutions.

(a) The literature^{1,2} reports evidence that the molar absorptivity of aqueous SO₂ solutions at 2750 Å passes through a maximum with increasing concentration, which, if true, would be evidence of some new species other than SO₂(aq) or HSO₃⁻, since only a steady increase in the molar absorptivity of SO₂ would be expected due to the repression of the ionization

with increasing SO₂ concentration. A careful repetition of these experiments has shown that the earlier results were in error and that the data, when corrected for activity coefficient changes, are quite in accord with Eq. (1).

(b) When SO₂ is added to concentrated HSO₃⁻ solutions, a yellow color appears³ although HSO₃⁻, SO₂, SO₃⁼, and S₂O₅⁼ are all colorless. As far as we know this species has never been identified. Preliminary spectrophotometric experiments indicate a dependence of the intensity of the yellow color on the concentrations of SO₂ and HSO₃⁻ which is consistent with a formula SO₂·S₂O₅⁼. The S₂O₅⁼ species can be considered to be a Lewis acid-base pair

The SO₂ sulfur in S₂O₅⁼ can now act as a base towards another SO₂ to form SO₂·S₂O₅⁼. The process could even be repeated, leading to chains

of SO₂ molecules attached to an SO₃⁼, but the data preclude the existence of chains of any significant length. It is hoped that more precise measurements will determine whether there is an appreciable amount of SO₂·S₃O₇⁼.

(c) An attempt is being made to measure more accurately the equilibrium constant for the reaction

since values in the literature are quite discordant. Efforts to measure the decrease in the HSO₃⁻ concentration from Raman spectra of HSO₃⁻ solutions were frustrated by limitations in the instrument available. A new and more accurate Raman spectrograph has been obtained and is now being tested and calibrated. The earlier experiments will be repeated with the expectation that a reliable value for the equilibrium constant will be obtained.

1. H. Ley and E. König, Z. Physik. Chem. (B) 41, 365 (1938).
2. Gmelins Handbuch der Anorganischen Chemie, 8th edition, 9, Part B, volume 2, p. 414 (1960).
3. F. Foerster, A. Brosch and Chr. Norberg-Schulz, Z. physik. Chem. 110, 435 (1924), p. 438.

2. RAMAN SPECTRA OF SULFITES, BISULFITES AND PYROSULFITES

B. Meyer, L. Peter and C. Shaskey

In connection with the studies of solutions of SO₂ and for purposes of identifying solids, it was desirable to have Raman spectra of a number of sulfite salts. The following previously known pure solid compounds were prepared and their Raman spectra measured: Na₂SO₃, K₂SO₃, Rb₂SO₃, Cs₂SO₃, (NH₄)₂SO₃, RbHSO₃, CsHSO₃, Na₂S₂O₅, K₂S₂O₅, Rb₂S₂O₅, Cs₂S₂O₅ and (NH₄)₂S₂O₅. The salts Li₂SO₃ and Li₂S₂O₅ were prepared for the first time and their spectra observed. In addition, the following isotopically substituted bisulfites and pyrosulfites were prepared and measured: CsDSO₃, CsHS¹⁸O₃, K₂³⁴S₂O₅, K₂S₂¹⁸O₅, Cs₂³⁴S₂O₅ and Cs₂S₂¹⁸O₅. Twelve of the 15 Raman frequencies of S₂O₅⁼ have been tentatively identified and the S and O isotope effects measured. The ion SO₃H⁻ with the proton attached to an oxygen has not yet been observed in any of the solids or in aqueous solution.

3. THE REACTION OF SO₂ WITH AMMONIA

B. Meyer and B. Mulliken

(a) The reagents were deposited individually and in mixture in various ratios, as pure substances, and in dilute rare gas matrices at 20K. Controlled warm-up experiments at 33K, 50K, 60K and 76K were used to study the diffusion of the reagents and the reaction after removal of the rare gas matrix. D₂O was employed to monitor traces of water in the pure system. The complex reactions which are fully reproducible will be analyzed in a forthcoming paper. The products include sulfites and pyrosulfites. At low pressure, the reaction products vaporize below -10°C, and probably decompose to NH₃ and SO₂. At atmospheric pressure, the reaction products are quite stable. In the reaction process at least two intermediates could be identified by their IR spectrum, but their structure is not yet established. Experiments with ¹⁵NH₃ and ³⁴SO₂ are now underway to determine the isotope shifts, and thus the atoms involved in the observed bonds.

(b) (partly with E. v. Deuster) A series of sealed Pyrex tubes were prepared to study the Raman spectrum of mixtures of liquid SO₂ and liquid ammonia with and without water at various temperatures. When the co-condensed gases warm up to -50°C, a slow reaction occurs. At -10°C, the reaction is quite exothermic and proceeds swiftly. At room temperature, the reaction product varies from a white solid, to a yellow solution, to a dark red solid, depending on the ratio of SO₂ to NH₃. The Raman spectra indicate a mixture of at least three products, which we hope to identify by the use of ¹⁵NH₃ and ³⁴SO₂ which are now at hand.

4. RESEARCH PLANS FOR CALENDAR YEAR 1977

R. E. Connick and E. von Deuster

The work on the HSO₃⁻-S₂O₅⁼ equilibrium constant will be finished and the identification of the yellow species in SO₂-S₂O₅⁼ solutions completed. Measurements will be made of the rate of exchange of oxygen between water solvent and SO₂, HSO₃⁻, S₂O₅⁼ and SO₃⁼ to clear up contradictory results currently in the literature. Studies will be started on the disproportionation of HSO₃⁻ and its oxidation by oxygen in aqueous solution. Both the thermal and photochemical paths of the latter reaction will be investigated. All of this work is aimed at providing a better understanding of SO₂ chemistry in connection with processes to reduce SO₂ pollution.

R. E. Connick and K. Klotter

Work will be continued on the identification of the two Ni(IDA)₂²⁻ species, where IDA is the iminodiacetate ion. Measurements will also be

made of the rate at which the oxygen of a carboxylate group attached to nickel ion is replaced by the other oxygen of the group. The research is designed to increase our knowledge of the dynamics of metal-ligand interactions.

R. E. Connick (with B. Alder at Livermore)

Molecular dynamics calculations will be continued on a model for substitution reactions on a metal ion in solution. The preliminary results in two dimensions will be extended to three dimensions.

B. Meyer and L. Peter

The isotopic work on pyrosulfite will be concluded and published. Our work will then be coordinated with that of Professor Connick's postdoctoral fellow to support their efforts to establish the equilibria of solutions of

and to unravel the contradictory kinetics.

B. Meyer

The isotopic work should establish the identity of the intermediates and products of the NH₃+SO₂ reaction and help reconcile the seemingly contradictory claims that NH₃ and SO₂ react, or merely form a loose adduct.

B. Meyer

A review with 1500 key references to sulfur chemistry relevant in connection with SO₂ abatement and possible new uses for abatement sulfur will be published in 1977 by Elsevier, Amsterdam. The excellent facilities of the UC Library were used to complete the literature search.

5. 1976 PUBLICATIONS AND REPORTS

R. E. Connick and Associates

Journals

1. B. Meyer, Elemental Sulfur, Chem. Rev. 76, 367 (1976).
2. B. Meyer, The Structures of Elemental Sulfur, Adv. Inorg. Chem. Radiochem. 18, 287 (1976).

Papers Presented

1. R. E. Connick and T. V. Rowland, Oxygen-17 NMR Studies of the Rate of Water Exchange from Partially Complexed Nickel Ion, presented at Sept. 1976 ACS Meeting in San Francisco.

b. Synthetic and Physical Chemistry

William L. Jolly, Principal Investigator

1. X-RAY PHOTOELECTRON SPECTROSCOPY*

a. π -Donor Relaxation in the Oxygen 1s Ionization of Carbonyl Compounds†

William L. Jolly and Theodore F. Schaaf

The oxygen 1s binding energies of compounds containing the keto group, $>C=O$, do not show a simple correlation with the electronegativities of the substituent groups. For example, the carbonyl oxygen 1s binding energies of methyl carbonate, formaldehyde, and carbonyl fluoride increase in the order $(CH_3O)_2CO < H_2CO < F_2CO$. The present study was carried out to test the hypothesis that this apparently anomalous behavior is due to different electronic relaxation energies in the photoionizations. We have determined the core binding energies of a wide variety of carbonyl compounds to provide sufficient data for systematic analysis. In our analysis of these data we have assumed that, in most of the compounds, core ionization of the carbonyl oxygen atoms involves "extra" relaxation energy due to π electron donation from the substituent groups. Using two different approaches, we have evaluated the relative π donor abilities of the various substituent groups.

The core binding energy of an atom in a molecule changes when other atoms in the molecule are replaced by different atoms or groups. These chemical shifts in binding energy are generally more pronounced the nearer the substituent groups are to the core-ionizing atom. This proximity effect can be seen in the carbon 1s binding energies of compounds of the type

As the groups, X, Y, and Z are changed, the binding energy of the CH_3 carbon atom changes much less than that of the CXYZ carbon atom. Figure 1 is a plot of the CH_3 binding energies

Fig. 1. Plot of CH_3 carbon 1s binding energies vs. CXYZ carbon 1s binding energies for compounds of the type CH_3CXYZ . Note that the vertical scale is twice as great as the horizontal scale. (XBL 759-7243)

against the CXYZ binding energies for 14 different compounds. This behavior is typical of simple compounds in which the atoms whose binding energies are being compared are joined by single bonds.

An entirely different result is obtained from a comparison of the oxygen and carbon binding energies of carbonyl compounds. A plot of the oxygen binding energies against the carbon binding energies (Fig. 2) shows that there is essentially

Fig. 2. Plot of carbonyl oxygen 1s binding energies vs. the corresponding carbonyl carbon 1s binding energies. The numbered points correspond to the following compounds: 1, anthrone; 2, dimethylformamide; 3, fluorenone; 4, p-chlorobenzaldehyde; 5, acetone; 6, vinyl acetate; 7, acrylaldehyde; 8, acetic anhydride; 9, pivaloyl chloride. (XBL 759-7244)

no correlation between these quantities. We believe the lack of correlation is caused by differences in the oxygen relaxation energies due to the different π -donor abilities of the groups attached to the carbonyl groups. If there were no shift in π electron density from the substituents to the oxygen of the carbonyl group, the oxygen core ionization would be represented by the equation

in which the ionized oxygen core is represented by the chemically equivalent fluorine core.

However, because of the high electronegativity of the fluorine atom, it is more realistic to represent the core-ionized molecule as a resonance hybrid:

We shall refer to the shift in π electron density which increases the extent to which the right-hand resonance structure contributes to the bonding of the core-ionized molecule as π -donor relaxation.

The straight line in Fig. 2 corresponds to the correlation expected for hypothetical molecules in which there is no π -donor relaxation in the carbonyl oxygen core ionization. Vertical deviations of the points in Fig. 2 from this line correspond to π -donor relaxation energies and are measures of the π -donor abilities of the groups.

We have used a second, entirely different method for estimating the "extra" relaxation energy associated with the oxygen core ionization of carbonyl compounds. The core binding energy of an atom can be calculated by the "transition-state" point-charge potential equation,

$$E_B = k(Q + Q_f - 1)/2 + (V + V_f)/2 + \ell \quad (1)$$

where Q is the initial charge on the atom, V is the Coulombic potential energy due to the other charged atoms in the molecule, Q_f and V_f are the values of Q and V for the core-ionized molecule, and k and ℓ are empirical constants. We have successfully correlated binding energies with Eq. (1) using atomic charges calculated by the CHELEQ electronegativity equalization method; the calculations for core-ionized molecules involved the equivalent-cores approximation. The k and ℓ values for oxygen were determined from data for compounds which have no ambiguities in bonding and no special relaxation energy effects. We have calculated the oxygen 1s binding energies of carbonyl compounds using these values of k and ℓ and assuming that the core-ionized molecules have the same simple valence-bond structures as the ground-state molecules (that is, assuming no π -donor relaxation). All of the calculated binding energies were greater than the experimental values; the differences are interpreted as π -donor relaxation energies. The values calculated in this way are similar to the values obtained from Fig. 2. The two sets of data are plotted against one another in Fig. 3 to show their correlation. Either set of π -donor relaxation energies may be used to compare the relative π -donor abilities of atoms and groups.

Swain and Lupton¹ have used a large number of kinetic, thermodynamic, and spectroscopic data to evaluate the magnitudes of the "resonance constant" R for a series of substituents. The scale of R values was set up such that negative

Fig. 3. Plot of π -donor relaxation energies calculated using CHELEQ charges and Eq. 1 vs. π -donor relaxation energies obtained from Fig. 2. (XBL 759-7245)

values correspond to substituents which are better π -donors than the hydrogen atom and positive values correspond to substituents which are better π acceptors than the hydrogen atom. In Fig. 4

Fig. 4. Plot of π -donor relaxation energies obtained from Fig. 2 for compounds of the type X_2CO vs. resonance constants for the groups X . Resonance constants are from Ref. 1.

(XBL 759-7246)

the π -donor relaxation energies evaluated from Fig. 2 for compounds of the type X_2CO are plotted against the R values for the X substituents. We believe that π -donor relaxation energies derived by the methods we have outlined should have numerous chemical applications.

*This work was largely supported by a National Science Foundation grant.

†Abstracted from J. Am. Chem. Soc. 98, 3178 (1976).

1. C. G. Swain and E. C. Lupton, Jr., J. Am. Chem. Soc. 90, 4328 (1968).

b. Core Binding Energies of Some Metal β -Diketonates and β -Diketones in the Vapor Phase*

Theodore F. Schaaf, Steven C. Avanzino, William L. Jolly, and Robert E. Sievers

X-ray photoelectron spectroscopy has been shown to be a useful technique for determining atomic charge distributions within molecules, particularly when applied to molecules in the gas phase. We have used this technique to obtain the core electron binding energies of a series of volatile tris β -diketonate complexes in order to study the valence electron distribution and bonding in these compounds. The β -diketonate ligands studied were hexafluoroacetylacetonate (hfa), trifluoroacetylacetonate (tfa), acetylacetonate (acac), and 2,2,6,6-tetramethyl-3,5-heptanedionate (thd). The compounds and measured core binding energies are listed in Table 1.

A chemical shift in core binding energy can be equated to the sum of three terms: (1) a term

proportional to the change in the charge of the atom that undergoes core ionization, (2) the change in electrostatic potential at the site of the core ionizing atom due to the charges of the other atoms in the two molecules, and (3) the change in the relaxation energy associated with core ionization.

$$\Delta E_B = k\Delta Q + \Delta V + \Delta E_R \quad (1)$$

In the case of the tris β -diketonates of aluminum, the molecular structure in the vicinity of the aluminum atoms is unchanged, and we believe it is a good approximation to assume that changes in the relaxation energy are zero for the aluminum 2p binding energies. Thus in this case we may write $\Delta E_B \approx k\Delta Q + \Delta V$. By making use of atomic charges calculated either by the CHELEQ method or the CNDO/2 method, we have shown that the shifts in the Al 2p binding energies can be accounted for mainly by changes in the electrostatic potential at the Al atom due to changes in the charges of the ligand atoms. The changes in the aluminum atom charge are very small.

It has been well-documented that core electron binding energy shifts can be closely correlated with chemical reaction energies. One might expect a good correlation between the aluminum binding energies in these chelates and the aqueous pK values of the corresponding β -diketones. A plot of these quantities against one another is shown in Fig. 5. The point for thd lies off the straight line because of what we believe is an abnormally high aqueous pK value for H(thd).

Table 1. Core binding energies (eV) of metal β -diketonates and β -diketones.

Compound	Metal 2p	O 1s	F 1s	C 1s			
				CF ₃	CO	CH	CH ₃
Al(thd) ₃	79.03	536.46			291.0		289.83 ^b
Al(acac) ₃	79.33	536.70			291.93	289.24	290.31
Al(tfa) ₃	80.36	537.75	693.72	298.05	293.00	290.30	391.09
Al(hfa) ₃	81.44	538.77	694.27	298.66	293.89	291.2	
V(hfa) ₃	522.34 ^a	538.64	694.29	298.64	293.74	290.93	
Cr(hfa) ₃	584.0 ^a	538.72	694.33	298.69	293.81	290.99	
Fe(hfa) ₃	----	538.75	694.37	298.94	294.14	291.33	
H(hfa)		{ 539.01 540.30	694.55	298.90	294.22	291.5	
H(acac)		{ 537.51 538.55			292.80		290.75 ^b

^a2p_{3/2} level.

^bCombination peak due to all non-carbonyl carbon atoms.

Fig. 5. A plot of Al 2p binding energies of tris β -diketonates vs. aqueous pK values of the corresponding β -diketones. (XBL 759-7167)

This diketone has two bulky *t*-butyl groups which may hinder hydration of the anion. Presumably a correlation of the binding energies with gas-phase pK values would not show this anomaly.

Among the aluminum complexes, the binding energies of a ligand atom of a particular type qualitatively follow the same trend as the binding energies of the aluminum atom, i.e., $\text{Al(hfa)}_3 > \text{Al(tfa)}_3 > \text{Al(acac)}_3 > \text{Al(thd)}_3$. This trend is that expected when one stepwise replaces the fluorine atoms of the CF_3 groups with the more electropositive hydrogen atoms and then with the more polarizable CH_3 groups. The decrease in binding energy is undoubtedly due to a reduction of both the absolute atomic charge and the electrostatic potential term and, in some cases, to increased relaxation (more negative E_p).

The binding energies of the carbon, oxygen, and fluorine atoms in the several hfa complexes change very little on going from one metal complex to another. Thus there is no evidence for participation of metal d orbitals in the bonding of the transition metal complexes. The same conclusion has been reached by other investigators with respect to acetylacetonate complexes on the basis of structural, magnetic, and spectroscopic data.

* Abstracted from J. Coord. Chem. 5, 157 (1976).

c. Prediction of Core Electron Binding Energies with a Four-Parameter Equation*

William L. Jolly and Albert A. Bakke

Chemical shifts in core electron binding energies can be equated to the energies of chemical reactions involving ground-state species.

For example, the difference between the carbon 1s binding energies of gaseous methane and gaseous carbon dioxide is practically the same as the energy of the following reaction.

The fact that there is a close correspondence between binding energy shifts and the energies of chemical processes suggests that it should be possible to predict binding energy shifts using the same sorts of correlations and empirical parameters that are used to predict the energies of chemical processes. In this research we show that it is possible to correlate core electron binding energy shifts by means of the relation

$$\Delta E_B = aF + bR \quad (1)$$

in which the parameters *a* and *b* are characteristic of the class of molecule and atom to which the binding energies pertain, and the parameters *F* and *R* are characteristic of substituent groups. The ΔE_B values are expressed in electron volts, relative to the binding energy of the molecule with a hydrogen atom as the substituent. Thus there are particular values of *a* and *b* which correspond to the carbon 1s binding energies of compounds of the type CH_3X , relative to methane. As an example, it is possible to predict the C 1s binding energy of methyl chloride relative to that of methane by substituting these values of *a* and *b* and the *F* and *R* values for the chloro group into Eq. (1).

We have considered 16 types of binding energy shifts. Five of these are carbon 1s shifts (for molecules of the type CH_3X , CF_3X , OCX_2 , CX_4 , and $\text{C}^*\text{H}_2\text{CHX}$), two are fluorine 1s shifts (for molecules of the type FX and F_2CX), and the remaining nine are core shifts for boron, silicon, germanium, tin, phosphorus, oxygen, chlorine, bromine, and iodine in molecules containing these elements. We have used data for the following ten substituents (in addition to hydrogen, the reference substituent): CH_3 , CF_3 , C_6H_5 , SiH_3 , GeH_3 , OCH_3 , F , Cl , Br , and I . The 16 types of binding energy shifts and ten substituents correspond to a total of 160 possible ΔE_B values. Only 92 of these values have been experimentally determined; they were used to evaluate the various *a*, *b*, *F*, and *R* values. In order to obtain a unique set of these parameters, four of them (the *F* and *R* values for CH_3 and the *a* and *b* values for CX_4) were arbitrarily fixed. Thus we obtained 92 equations with 48 parameters to be determined. The values of the parameters, determined by a least-squares computer program, are given in Tables 1 and 2. The Gauss criterion for closeness of fit was used, that is, the parameters were chosen to minimize the sum of the squares of the deviations between experimental and calculated values.

The values of the four fixed parameters were chosen so that (1) the trend in *F* values qualita-

Table 1. Values of F and R

Substituent	F	R
CH ₃	(0.000)	(-2.00)
CF ₃	0.486	-3.07
C ₆ H ₅	-0.286	-0.01
SiH ₃	-0.230	-0.02
GeH ₃	-0.258	-0.70
OCH ₃	0.722	-7.61
F	1.787	-13.88
Cl	0.959	-7.68
Br	0.624	-4.53
I	0.451	-4.28

Table 2. Values of a and b.

Class of molecule	a	b	b/a
BX ₃	7.21	0.525	0.073
CH ₃ X	1.97	0.037	0.019
C*F ₃ X	3.76	0.323	0.086
OC*X ₂	4.58	0.221	0.048
CX ₄	(8.00)	(0.250)	0.031
C*H ₂ CHX	4.11	0.492	0.120
SiX ₄	8.22	0.698	0.085
GeX ₄	7.34	0.600	0.082
SnX ₄	7.62	0.651	0.085
PX ₃	7.21	0.576	0.080
O*CX ₂	8.27	0.985	0.119
FX	6.85	0.726	0.106
CF ₃ *X	2.67	0.280	0.105
CIX	5.07	0.565	0.111
BrX	3.76	0.576	0.153
IX	3.46	0.402	0.116

tively resembles that for electronegativity or σ electron withdrawing power (e.g., the F value for the fluorine atom is greater than that for the methyl group), (2) the trend in R values qualitatively resembles that for π electron withdrawing power (e.g., the R value for a good π donor such as the fluorine atom is more negative than that for a relatively poor π donor such as the methyl group), and (3) all the a and b values are positive. The last restriction is reasonable if one wishes to interpret the a and b values as absolute measures of the sensitivity of the core-ionizing atoms to respectively σ and π interactions with substituent groups. The ratio b/a, given in Table 2, may be taken as a measure of

the π electron sensitivity, relative to the σ electron sensitivity, of the core-ionizing atoms. High values of b/a were found for atoms which can accept negative formal charge from substituents, as in the case of the oxygen atoms of ketones and the β carbon atoms of vinyl compounds.

Core ionization of such atoms probably involves a relatively large amount of electronic relaxation in which electron density is shifted to the core-ionizing atom from the substituents. The average deviation between the experimental and calculated binding energies is ± 0.20 eV; the standard deviation (calculated on the basis that all the a, b, F, and R parameters are variables) is ± 0.37 eV. These deviations are quite reasonable in view of the fact that many of the experimental ΔE_B values are uncertain by as much as ± 0.3 eV.

Obviously Eq. (1) can be very useful for predicting unknown core binding energies. As a bonus, the F and R values in Table 1 give us information regarding the electronegativities and π donor/acceptor abilities of the substituents. The F and R values are also useful for correlating the energies of any general process in which a positive charge forms on an atom. One process of this type is the ionization of a lone-pair electron such as a nonbonding valence electron of a halogen atom in a molecular halide. We have shown that literature values of the valence shell lone-pair ionization potentials of various chlorides and iodides can be correlated using Eq. (1) and the F and R values from Table 1. The least-squares evaluated parameters are, in the case of the 3p ionization potentials of chlorides, $a = 4.59$ and $b = 0.57$, and for the 5p_{1/2} ionization potentials of iodides, $a = 2.50$ and $b = 0.36$. The standard deviations are 0.25 and 0.27 eV; the average absolute deviations are 0.19 and 0.18 eV, and the correlation coefficients are 0.957 and 0.799, respectively.

Another general process for which energies can be correlated with the F and R values is the addition of a proton to a lone pair of electrons. We have successfully correlated the proton affinities (PA) of amines, XNH_2 , covering the extreme variety of substituents of Table 1, using the relation

$$-\Delta(\text{PA}) = aF + bR.$$

In this case the least-squares evaluated parameters a and b are 1.07 and 0.07, respectively. The standard and average absolute deviations

are 0.22 and 0.15 eV, respectively, and the correlation coefficient is 0.890.

The F and R values in Table 1 resemble in some respects the corresponding F and R values of Swain and Lupton.¹ However, the sets are fundamentally different (they cannot even approximately be transformed into one another) for two reasons. First, the F and R values apply only to gaseous species and thus are independent of solvent effects that undoubtedly affect the F and R values. Second, the F and R values are strictly applicable only to processes in which a localized positive charge develops. The F and R values are therefore principally affected by the donor abilities of the substituents and are relatively independent of the acceptor abilities. (A good donor is not necessarily a poor acceptor, and vice versa.) On the other hand, the F and R values were set up to be applicable to a wide variety of processes, including both nucleophilic and electrophilic reactions. Hence the F and R values reflect both donor and acceptor characteristics. Probably these facts can be used to explain the fact that the R value for the CF_3 group is negative, whereas the corresponding R value is positive. In a core ionization, the π acceptor ability of a substituent is relatively unimportant compared to its π donor ability. Hence the low negative R value for CF_3 , indicating that CF_3 is a fairly poor π donor, is reasonable. However, in many other chemical processes, the strong π acceptor ability of CF_3 is important. The positive R value reflects this ability. Obviously F and R values represent a compromise in the measure of donor and acceptor properties. It is significant that lone pair ionization potential data and proton affinity data are very poorly correlated if F and R values are used instead of F and R values.

* Abstracted from J. Am. Chem. Soc. 98, 6500 (1976).

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d. A Study of Bridging and Terminal Carbonyl Groups in Transition Metal Complexes by X-Ray Photoelectron Spectroscopy*

Steven C. Avanzino and William L. Jolly

It is well-known that there are two principal modes of coordination of the carbon monoxide ligand in transition metal carbonyls: terminal coordination, to a single metal atom, and bridging coordination, to two or more metal atoms. Aside from direct structure determination, as by x-ray and electron diffraction, the main, and perhaps only, physical methods which have been used to distinguish these modes of coordination are infrared and Raman spectroscopy and carbon-13 NMR. In this research we have shown that it is possible to distinguish and identify terminal and bridging carbonyl groups by means of x-ray photoelectron spectroscopy in the oxygen 1s region. Our results help clarify the interpretation of oxygen 1s XPS spectra of carbon monoxide adsorbed on metal surfaces.

Previous attempts to study the x-ray photoelectron spectra of solid carbonyl complexes containing both bridging and terminal CO ligands have been unsuccessful because of extensive surface decomposition of the samples under intense x radiation. Therefore we restricted this work to the study of volatile molecular compounds in the gas phase. The O 1s spectrum of acetylpentacarbonylmanganese is shown in Fig. 6. The fact

Fig. 6. The oxygen 1s spectrum of $\text{CH}_3\text{COMn}(\text{CO})_5$. (XBL 763-705)

that we were able to resolve this spectrum clearly into a band due to the five terminal CO ligands ($E_B = 539.75$ eV) and a band due to the keto group ($E_B = 537.01$ eV) encouraged us to study molecules containing both terminal and true metal-bridging CO ligands. This result also suggested that we would find the O 1s binding energies of bridging carbonyls to be lower than those of ionizations. The possibility of $\text{d}\pi$ electron transfer from the metal during the ionization is present in both cases.

In recent years Yates et al.¹ and Atkinson et al.² have identified several forms of carbon

monoxide adsorbed on tungsten and molybdenum surfaces by means of oxygen 1s photoelectron spectra. A peak at relatively low binding energy, formed principally at low temperatures and low surface coverage, has been identified with the "virgin" state of CO. This state is believed to consist of CO coordinated through the carbon atom to two or more metal atoms and, as such, is analogous to bridging carbonyl groups in molecular metal carbonyls. A band at relatively high binding energy, corresponding to weakly-bound CO, which can still be desorbed from the surface, is identified with " α " CO in the case of tungsten and " γ " CO in the case of molybdenum. These states presumably consist of CO coordinated through the carbon atom to only one metal atom and are thus analogous to the carbon monoxide in a terminal carbonyl group. The breadth of the α and γ bands suggests different degrees of back-bonding due to differences in the sites of the attached metal atoms. These structural interpretations of the virgin, α and γ states of adsorbed CO are in qualitative agreement with our results; that is, we agree that the O 1s binding energy of a multiply-coordinated CO molecule is lower than that of a singly-coordinated carbonyl.

The O 1s spectrum of the binuclear complex $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ (containing two terminal CO ligands and two bridging CO ligands) is shown in Fig. 7. The overall fwhm of the band is much

Fig. 7. The oxygen 1s spectrum of $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$. (XBL 763-704)

greater than generally found for O 1s peaks and we feel justified in our deconvolution of the band into two peaks of reasonable fwhm (1.32 and

1.28 eV) and equal area, separated by 1.2 eV. We believe, on the basis of our data for $\text{CH}_3\text{COMn}(\text{CO})_5$ and $\text{Co}_4(\text{CO})_{12}$ (see below), that the peak of lower binding energy corresponds to the bridging CO ligands. A successful spectrum was obtained from $\text{Co}_4(\text{CO})_{12}$, which contains nine terminal CO ligands and three bridging CO ligands. The spectrum, shown in Fig. 8, has a

Fig. 8. The oxygen 1s spectrum of $\text{Co}_4(\text{CO})_{12}$. (XBL 763-707)

peak at high binding energy corresponding to free carbon monoxide formed by some thermal and x-ray decomposition of the sample. The band at lower binding energy, attributed to $\text{Co}_4(\text{CO})_{12}$, has been resolved into two peaks with relative areas of 3:1 and separated by 1.25 eV. The lower binding energy corresponds to the bridging carbonyls.

The fact that a lower O 1s binding energy was found for bridging carbonyls than for terminal carbonyls is what one might expect assuming greater back-bonding in the bridging carbonyls. It is also the expectation from simple valence bond formulas in which the terminal carbonyl is represented with no back-bonding and the bridging carbonyl is represented by a simple keto structure. The oxygen atom with the lower formal

charge would be expected to have the lower 1s binding energy. Of course considerable relaxation is undoubtedly associated with both of these O 1s coordinated CO molecule. In this respect our results confirm the assignments of the XPS spectra of adsorbed CO.

The C 1s spectrum of acetylpentacarbonylmanganese is shown in Fig. 9. The spectrum is

Fig. 9. The carbon 1s spectrum of $\text{CH}_3\text{COMn}(\text{CO})_5$. (XBL 763-706)

readily resolved into three peaks having appropriate relative intensities corresponding to the five CO ligands, the keto group, and the methyl group. According to the resolved spectrum, the binding energy of the keto carbon atom is less than that of the carbon atoms of the five carbonyl groups. This result strongly suggests that the positive charge of the keto carbon atom is less than that of any of the CO ligand carbon atoms. This result is contrary to recent calculations of Block et al.⁵

* Abstracted from J. Am. Chem. Soc. 98, 6505 (1976).

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e. The Core Electron Binding Energies of Oxygen Difluoride*

J. W. Koepke and W. L. Jolly

All of the oxygen 1s binding energies which have been reported for oxygen-containing compounds

are lower than that of molecular oxygen. In all of the oxygen compounds which have been studied, the oxygen atoms are bonded to less electronegative atoms and are probably negatively charged. In this study, we determined the oxygen 1s and fluorine 1s binding energies of gaseous OF_2 , in which the oxygen atom is believed to be positively charged.

The experimental binding energies are listed in Table 1. The value for O_2 is the weighted average of the two peaks of the spin doublet and is in good agreement with the value 543.5 eV calculated from the data of Siegbahn et al.¹ The value for F_2 was reported by Carroll et al.² The oxygen 1s binding energy of OF_2 is 1.61 eV more positive than that of O_2 and is the highest oxygen 1s binding energy known. The fluorine 1s binding energy of OF_2 is higher than that of most fluorine compounds; however a few compounds, in which fluorine atoms are bonded to very electronegative or π -electron-withdrawing groups, have still higher fluorine 1s binding energies. For example, CF_4 , COF_2 , and NOF_3 have fluorine 1s binding energies of 695.36, 695.26, and 695.13 eV, respectively.

The shift in the fluorine 1s binding energy between OF_2 and F_2 may be expressed by the point-charge potential equation

$$\Delta E_B = kQ_F + \frac{Q_F}{R_F} - \frac{2Q_F}{R_O} \quad (1)$$

in which k is a constant to be evaluated theoretically, Q_F is the fluorine atom charge, and R_F and R_O are the distances from one fluorine atom to the center of charge on the other fluorine atom and the oxygen atom, respectively. In writing Eq. (1), we make the assumption (which we believe to be very reasonable) that the relaxation energy associated with the F 1s ionization of OF_2 is the same as that of F_2 . We use the equivalent cores approximation to calculate $k = 20.83$, i.e., we assume that k is one-half the energy of the following reaction

Table 1. Experimental binding energies.

Compound	E_B , eV	
	O 1s	F 1s
OF_2	545.19	694.93
O_2	543.58	
F_2		696.71 ^a

^aFrom Ref. 2.

As a first approximation, we shall assume that R_F and R_O are equal to the F-F and F-O internuclear distances, respectively. Equation (1) can then be solved by substitution of the calculated value of k , experimental values of the internuclear distances, and the value of ΔE_B calculated from data in Table 1. We thus calculate $Q_F = -0.26$ and $Q_O = +0.52$. These values are considerably greater in absolute magnitude than the values $Q_F = -0.12$ and $Q_O = +0.23$ obtained by Rothenberg and Schaefer³ from a Mulliken population analysis based on *ab initio* SCF calculations for OF_2 . We believe our calculated charges are too large because of the use of internuclear distances for R_F and R_O . In OF_2 , the negative charge of each fluorine atom is concentrated on the side of the atom farthest from the oxygen atom, and the positive charge of the oxygen atom is concentrated on the side farthest from the fluorine atoms. Thus the distances from a given fluorine nucleus to the effective centers of charge of the other two atoms (R_F and R_O) are greater than the corresponding internuclear distances. We find that if we use R_F and R_O values equal to the internuclear distances plus 0.5 Å, the charges calculated from Eq. (1) are considerably lower, viz, $Q_F = -0.16$ and $Q_O = +0.32$. Clearly the problem of determining the effective centers of charge of atoms deserves further study.

* Abstracted from a paper to be published in J. Electron Spectrosc. Rel. Phen. 9, 413 (1977).

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2. SYNTHETIC AND MECHANISTIC STUDIES

a. Boron Hydride Chemistry

Thomas S. Briggs and William L. Jolly

Synthetic procedures for the new compound diamminoborane, $BH(NH_2)_2$, were investigated. The best yields (about 10%) were obtained by passing ammonia through a coil containing 0.6 g of NH_3BH_3 immersed in a hot oil bath. The hydrogen evolved during the pyrolysis is continuously pumped off, and the product and excess ammonia are collected in a liquid nitrogen trap. The product is separated from the ammonia by fractional condensation using a -104° trap.

A convenient synthesis for NH_3BH_3 was developed. Sodium borohydride is mixed with a slight excess of ammonium sulfamate in liquid ammonia, and the

solution is allowed to warm to room temperature while rapidly stirring with ether. Upon filtration and removal of ether, a 67% yield of NH_3BH_3 is typically obtained. A kinetic study of the hydrolysis of NH_3BH_3 in aqueous solutions buffered around pH 5 is in progress. It has been shown that NH_3BH_3 reacts with sodium-ammonia solutions to form $NaNH_2BH_3$ and that the latter can be reconverted to NH_3BH_3 by treatment with an ammonium salt. NH_3BH_3 has considerable potential as a moderately strong reducing agent in aqueous systems.

b. Germanium Chemistry

Duck J. Yang and William L. Jolly

We have shown that hot, strongly alkaline solutions of $GeH_3CO_2^-$ decompose to form a brown solid identical to that formed by treatment of germanous hydroxide, $Ge(OH)_2$, with alkaline solutions. Infrared spectra show this brown material to contain Ge-H and Ge-O-Ge bonds, and we believe the material is a polymer having a structure like the following

We have found that cold ($\sim -40^\circ$) aqueous acid solutions of GeH_3CO_2H decompose to give a white precipitate and CO gas with no germane or hydrogen. This result indicates that, in such solutions, stoichiometric $(GeH_2)_x$ forms:

Heretofore we had obtained GeH_4 gas and a solid of approximate composition $GeH_{0.6}$ and had only been able to infer the intermediate formation of GeH_2 in the reaction.

c. Nitrogen Chemistry

John Illige and William L. Jolly

We have studied the mechanism of the thermal decomposition of the blue gas nitrosyl cyanide,

using ONCN in which the terminal nitrogen atom is labelled with ^{15}N . Most of the ^{15}N ended up in the cyanogen and in the terminal nitrogen atom of the N_2O , suggesting the mechanism

However, the detailed distribution of ^{15}N among the products is not entirely explained by this mechanism. At least one other process must be involved, and we are in the process of interpreting the data.

3. RESEARCH PLANS FOR CALENDAR YEAR 1977

William L. Jolly

a. X-Ray Photoelectron Spectroscopy. We believe that it should be possible to use O 1s binding energies to measure the degree of back-bonding in transition metal carbonyls. Therefore we are attempting the correlation of O 1s binding energies of such compounds with other physical chemical data (e.g., C-O stretching frequencies) that are supposed to be measures of back-bonding. We hope to obtain C 1s and O 1s binding energies for carbonyl groups which are bonded "sideways" to metal atoms. Such data will be helpful in interpreting XPS spectra of carbon monoxide chemisorbed in various ways on catalytic surfaces.

We plan to analyze critically the known core binding energies and the corresponding appropriate heats of formation to determine the accuracy which can be expected of the "equivalent cores" approximation and to permit the accurate calculation of heats of formation of gaseous cations from binding energies. Other projects anticipated or in progress are (1) a study of transition metal mixed valence compounds to help elucidate the interaction between the metal atoms in such systems, (2) a study of organometallic compounds to clarify the nature of metal-ligand bonds (and their analogs in catalyst systems), and (3) a detailed study of charge distribution in some simple compounds such as ClF .

b. Synthetic and Mechanistic Studies. We will probably complete the physical and chemical characterization of NH_3BH_3 and $\text{BH}(\text{NH}_2)_2$. A study of the reactive intermediates in the acid hydrolysis of B_3H_8^- will be studied; this study is expected to uncover highly reactive species which can be used as synthetic intermediates. Preliminary works indicates that the germal ion, GeH_3^- , reacts with sulfur to form GeH_3S^- . This species should be a useful reagent for the synthesis of many new sulfur-germanium compounds. Analogous reagents can probably be generated by the reaction of GeH_3^- with other nonmetals, such as Se, P, and the halogens.

4. 1976 PUBLICATIONS AND REPORTS

William L. Jolly and Associates

Journals

1. W. L. Jolly and S. C. Avanzino, Photoelectron Spectroscopy, X-Ray, 1976 McGraw-Hill Yearbook of Science and Technology.
2. W. L. Jolly and T. F. Schaaf, π -Donor Relaxation in the Oxygen 1s Ionization of Carbonyl Compounds, *J. Am. Chem. Soc.* 98, 3178 (1976), LBL-4186.
3. T. F. Schaaf, S. C. Avanzino, and W. L. Jolly, Core Binding Energies of Some Metal β -Diketonates and β Diketones in the Vapor Phase, *J. Coord. Chem.* 5, 157 (1976), LBL-4176.
4. W. L. Jolly and A. A. Bakke, Prediction of Core Electron Binding Energies with a Four-Parameter Equation, *J. Am. Chem. Soc.* 98, 6500 (1976), LBL-4934.
5. S. C. Avanzino and W. L. Jolly, A Study of Bridging and Terminal Carbonyl Groups in Transition Metal Complexes by X-Ray Photoelectron Spectroscopy, *J. Am. Chem. Soc.* 98, 6505 (1976), LBL-4923.
6. J. W. Koepke and W. L. Jolly, The Core Electron Binding Energies of Oxygen Difluoride, *J. Electron Spectrosc. Rel. Phen.* 9, 413 (1976), LBL-4957.

Papers Presented

William L. Jolly

Talks describing "Studies of π Bonding by X-Ray Photoelectron Spectroscopy" were given at the following times and places:

1. Feb. 6, Chemistry Dept., University of Southern California, Los Angeles.
2. April 28, Chemistry Dept., University of Durham, Durham, England.
3. May 4, Chemistry Dept., University of Sussex, Brighton, England.
4. May 31, Institute of Physics, University of Uppsala, Sweden.
5. June 3, Institute of Inorganic Chemistry, University of Göttingen, Göttingen, Germany.
6. June 8, Institute of Inorganic Chemistry, University of Heidelberg, Heidelberg, Germany.
7. June 10, Institute of Inorganic Chemistry, University of Würzburg, Würzburg, Germany.
8. June 14, Institute of Inorganic Chemistry, University of Stuttgart, Stuttgart, Germany.

9. June 16, Institute of Inorganic Chemistry,
University of Frankfurt, Frankfurt, Germany.

10. Sept. 24, Chemistry Dept., San Francisco
State University, San Francisco.

11. Oct. 27, Chemistry Dept., University of
California, Santa Cruz.

12. A talk describing our "Work on Inorganic
Synthesis" was given on May 20, Chemistry Dept.,
University of Sussex, Brighton, England.

LBL Reports

1. John D. Illige, Attempts to Prepare Nitrosyl
Oxide and a Study of the Decomposition of Nitrosyl,
(Ph. D. thesis), LBL-5196, July 1976.

2. W. L. Jolly, Inorganic Applications of X-Ray
Photoelectron Spectroscopy, LBL-5705, October
1976.

3. W. L. Jolly, S. C. Avanzino, and R. R. Rietz,
The Use of Oxygen 1s Binding Energies and
Multiplicity-Weighted C-O Stretching Frequencies
to Measure Back-Bonding in Transition Metal
Carbonyl Complexes, LBL-5708, October 1976.

4. W. L. Jolly and C. Gin, The Correlation of
Core Replacement Energies with Nonbonding s
Electron Density, LBL-5726, October 1976.

5. W. L. Jolly and C. Gin, The Calculation of
Heats of Formation of Gaseous Cations from Core
Electron Binding Energies, LBL-5728, October
1976.

c. Electrochemical Systems

John Newman, Principal Investigator

1. HIGH TEMPERATURE EROSION-CORROSION OF Fe-Ni-Cr ALLOYS UNDER COAL GASIFIER CONDITIONS

B. A. Gordon and J. Newman

Failure of high-temperature alloys under coal gasifier conditions occurs from a combination of the growth of non-protective scales and removal of the scales by eroding particles. Growth of the scale can be modeled as a chemical reaction which include mass transport across a growing porous layer. Modeling of such porous layers has been done for electrochemical systems.¹ The erosion of the layers is a complex function of particle velocity, surface temperature, impact angle, rate of impact, and hardness of surface.²

We will obtain data on the kinetics of erosion-corrosion of 310 stainless steel and tie this in with the theoretical model.

1. J. Newman, J. Electrochem. Soc. 119, 186 (1972).
2. D. McFadden, Ph.D. thesis, Dept. of Mechanical Engineering, University of California, Berkeley, in preparation.

2. POTENTIAL-SELECTIVE DEPOSITION OF COPPER FROM SOLUTIONS CONTAINING IRON AND COMPLEXED WITH CHLORIDE

Ralph White, James A. Trainham, John Newman, and Thomas W. Chapman

The hydrometallurgy of copper may involve leaching of the metal from its ore with an aqueous solution containing cupric and ferric chloride. The subsequent deposition of copper from such a process stream is modeled here in an idealized electrochemical cell with a rotating-disk electrode. The potential distribution and concentration profiles within the diffusion layer are predicted for given potential differences between the electrode and the solution.¹

The cuprous ion, which is formed by the reduction of the complexed cupric ion at the electrode, is stabilized in the chloride solution and can react either at the electrode or with ferric species within the diffusion layer. The assumptions that this homogeneous reaction is fast and irreversible generates a reaction plane, whose position is shown in the concentration and potential profiles. In addition, the position of the reaction plane is plotted as a function of the potential difference between the electrode and the adjacent solution. Predicted current-potential and current efficiency-potential curves are also reported. Finally, the iron contamination of the deposited copper is estimated to be less than 10^{-5} at.% for some cases.

1. Ralph White, et al., LBL-4986, Aug. 1976.

3. DISSOLUTION RATE OF CADMIUM HYDROXIDE

Ralph White and John Newman

Cadmium hydroxide forms on the negative electrode during discharge of a nickel-cadmium battery. Upon charging, one possible cadmium recovery path is dissolution of $\text{Cd}(\text{OH})_2$ followed by reduction of the soluble species. An attempt to measure the dissolution rate of $\text{Cd}(\text{OH})_2$ with a rotating ring-disk electrode has as yet been unsuccessful.

The experimental cell consisted of a Pine Instrument Company PIR Rotator, a DT6 platinum ring-disk electrode electroplated with cadmium, a 6.9 M KOH solution, a 3 in. $\times$ 3 in. $\times$ 1/8 in. nickel sheet counter-electrode, and a mercury/mercuric oxide reference electrode. A Wenking potentiostat was used to polarize the electrode.

The experimental procedure consisted of two steps. First, $\text{Cd}(\text{OH})_2$ was formed galvanostatically on the disk; and, second, a limiting current curve was sought unsuccessfully for the reduction of the soluble species on the ring.

The reason for the failure of this technique may be that the cadmium hydroxide layer was too thick. That is, the $\text{Cd}(\text{OH})_2$ may have flaked off in addition to dissolving. Typically, the cadmium hydroxide layer was formed by passing 25 mA/cm² for about 105 minutes at a rotation speed of 2500 rpm during which the cell was open to the atmosphere and immersed in a $25 \pm 0.05^\circ\text{C}$ water bath.

4. SIMULTANEOUS REACTIONS ON A ROTATING-DISK ELECTRODE

Ralph White and John Newman

Multiple reactions at a rotating-disk electrode are modeled. The governing equations are used to generate a parameter which can be used to predict the effect of a side reaction on the limiting-current curve of a main reaction. Various predicted current-voltage curves for a main reaction followed by a side reaction illustrate the importance of this parameter.

Current, potential, and surface concentration distributions on the disk are presented for copper deposition from a sulfuric acid solution with generation of dissolved hydrogen gas as the side reaction. The distributions illustrate that in some cases the main reaction can be below its limiting rate at the center of the disk while dissolved hydrogen gas is being formed near the edge. Finally, predicted and measured limiting curves for this system are compared.

5. THERMODYNAMICS OF MULTICOMPONENT AQUEOUS SOLUTIONS CONTAINING VOLATILE WEAK-ELECTROLYTES*

Thomas J. Edwards, Toshikata Hakuta, John Newman, and John M. Prausnitz

A knowledge of the vapor-liquid equilibrium of volatile weak-electrolytes is required for the proper design of pollution abatement processes for new chemical processes. In an effort to extend the available data base, an apparatus has been constructed allowing the sampling and analysis of a three-phase system (vapor, hydrocarbon, and aqueous) containing ammonia, carbon dioxide, and hydrogen sulfide up to 175°C and 30 atmospheres. The results of these experiments are being used in a theoretical model of these systems. Equations are used which are appropriate for the activity of weak electrolytes at high concentrations (as proposed by Pitzer).¹

* Work supported by National Science Foundation. T. Hakuta is supported by The Science and Technology Agency of Japan.

1. K. S. Pitzer, J. of Phys. Chem. 77, 268 (1973).

6. EFFECT OF DIFFUSIONAL RESISTANCE UPON GAS CHROMATOGRAPHY IN CAPILLARY COLUMNS*

Thomas J. Edwards and John Newman

A theoretical investigation¹ indicates the effect stationary-phase mass-transfer resistance has on thermodynamic properties as obtained from chromatographic measurements utilizing open-tubular columns. The model applies to a wide range of experimental conditions. Parameters for the system are: carrier-gas flow rate, column length, solute diffusivity, absorbent layer thickness, ratio of tube radius to absorbing layer thickness, and the true Henry's constant. A plot has been developed which allows simple determination of the true Henry's constant from the experimentally observed Henry's constant.

The analysis predicts lower true Henry's constants than those predicted by previously presented reduction methods. As a result, Flory's χ parameter determined by packed and by capillary columns for the benzene- and cyclohexane-polyisobutylene systems are brought into better mutual agreement.

The analysis indicates that both the diffusivity and the true Henry's constant for a given solute-solvent system may be determined from a single set of chromatographic experiments.

* Work supported by National Science Foundation.

1. Submitted to Macromolecules.

7. CALCULATION OF DISTILLATION COLUMNS AT THE OPTIMUM FEED PLATE LOCATION

Donald N. Hanson and John Newman

A method is shown¹ employing Underwood's equations for calculation of distillation columns with the feed plate at the optimum location. Calculation of examples shows that the common rules of thumb for location of the feed plate are often unreliable, particularly at reflux values near minimum reflux. A Fortran computer program for the calculation, general for up to 20 components, is available from the authors.

1. Donald N. Hanson and John Newman, Calculation of Distillation Columns at the Optimum Feed Plate Location, Ind. Eng. Chem. Process Design and Development, to be published.

8. FLOW-THROUGH POROUS ELECTRODES

John Newman and William Tiedemann

High specific interfacial areas, intimate contact of the electrode with the electrolytic solution, and mechanical simplicity make flow-through porous electrodes attractive as electrochemical reactors for recovery of metals, synthesis of chemicals, and storage of energy. Emphasis is given¹ to the quantitative design principles by which the production rate, subject to a constraint of selectivity under conditions of controlled-potential electrolysis, can be related to mass-transfer limitations and to the influence of the ohmic potential drop.

1. John Newman and William Tiedemann, Flow-through Porous Electrodes, LBL-4942, March 1976, Advances in Electrochemistry and Electrochemical Engineering, to be published.

9. TRANSIENT RESPONSE OF POROUS BATTERY ELECTRODES

Hiram Gu, Douglas N. Bennion, and John Newman

A mathematical model which describes the operation of porous, battery electrodes has been developed.¹ It includes short-time transient behavior of electrolyte concentration, porosity, current distribution, reaction rate, and detailed solution-diffusion descriptions of a sparingly soluble reactant. Calculations were made for constant-current (50 mA/cm² and 25 mA/cm²) charging and discharging of Ag/AgCl electrodes. Results of calculations indicate that the concentration of the electrolyte, KCl, inside the porous electrode plays an important role in the performance of the electrode. During charging, the electrolyte concentration falls in the depth of the electrode, thereby decreasing the solution electrical conductivity. Reaction penetration depth on charging is very shallow, less than 0.3 mm, for the current densities investigated. On discharging, the electrolyte concentration in the depth of the electrode increases. Consequently, the electrical conductivity of the solution as well as the solubility of AgCl increases. A high reaction rate in the depth of the electrode is possible even at high-current discharge. A

charge utilization of over 90% is predicted if the charge is stored uniformly by employing a slow charging rate.

1. Hiram Gu, Douglas N. Bennion, and John Newman, Analysis of Porous Electrodes with Sparingly Soluble Reactants. III. Short Time Transients, J. Electrochem. Soc. 123, 1364 (1976).

10. EXACT LOW-TEMPERATURE SECOND-VIRIAL EXPANSIONS

C. J. Radke and John Newman

At high energies or low temperature, the use of rigorous series expressions of virial coefficients to obtain parameters of the intermolecular potential is difficult because of the slow convergence of the series. We develop exact low-temperature expansions based on the dominance of the behavior of the intermolecular potential-energy function in the region near the potential minimum. This procedure is applied also to two-dimensional virial coefficients applicable to adsorption.

11. MASS TRANSFER IN TURBULENT FLOW BETWEEN ROTATING CYLINDERS WITH SMALL SEPARATION GAPS

Charles M. Mohr, Jr. and John Newman

The results of an experimental study of mass transfer in turbulent cylindrical couette flow are presented¹ and compared to the predictions of a model based upon the empirical "universal velocity profile" derived for turbulent pipe flow. The gap distance between the nickel electrodes was varied from nine percent to less than two percent of the inner cylinder radius, and the experiments were performed using the ferricyanide-ferrocyanide redox reaction in KOH and NaOH/Na₂SO₄ supported electrolytes. The mass-transfer rates were found to lie below those predicted by correlations of data from wider gap experiments and displayed fundamental differences from the predictions of the proposed model. For the limited range of parameters, Re (Reynolds number) and κ (gap ratio), studied, the data (for a Schmidt number of 1661) are fitted to within $\pm 4\%$ by the equation

$$St = (0.001177 - 0.000983\kappa)Re_i^{-0.2}$$

where St is the dimensionless Stanton number. The results suggest that the "universal velocity profile" is not applicable to this flow and that further modeling advances for this system must be based upon an improved knowledge of the nature of rotating turbulent flows.

1. Charles M. Mohr, Jr. and John Newman, Mass Transfer in Turbulent Flow Between Rotating

Cylinders with Small Separation Gaps, LBL-5136, May 1976, Electrochimica Acta, to be published.

12. SECONDARY CURRENT DISTRIBUTION WITH PASSIVATION KINETICS ON A ROTATING DISK ELECTRODE

Clarence G. Law and John Newman

Since the hydrodynamics of a rotating disk are well understood, the disk can be utilized to calculate mass transfer of species and the potential distribution for corrosion reactions. Work has begun on the secondary current distribution with passivation kinetic expressions. Ferrous metals under various conditions exhibit a discontinuous potential-current curve. The discontinuity is attributed to the formation of a thin coherent film which passivates the surface and protects it from further corrosion.

13. RING ELECTRODES

Peter Pierini and John Newman

The characteristic current distributions for rotating ring electrodes were computed for a number of important cases involving laminar flow. The primary current distribution was obtained following Miksis and Newman,¹ and was compared to the limiting current distribution given by Levich.² The resistance for the ring primary current was tabulated. The current distribution for a ring electrode operating at a fraction of the limiting current which requires consideration of ohmic effects, kinetics and mass transfer was computed for linear kinetics, Tafel kinetics and complete overpotential expressions. Thick rings were compared to disks and thin rings were contrasted with infinitely long rectangular planar electrodes with channel flow. The applicability of thin ring electrodes to the study of high current density processes was also demonstrated.

1. J. J. Miksis, Jr. and J. Newman, J. Elect. Soc. 123, 1030 (1976).
2. V. G. Levich, *Physicochemical Hydrodynamics*, Prentice Hall, Inc., p. 109 (1962).

14. COMPUTED COLLECTION EFFICIENCIES FOR RING-DISK ELECTRODE SYSTEMS

Peter Pierini and John Newman

Collection efficiencies are measured by generating a chemical species on a disk electrode which could be operated anodically and then reversing the reaction on the ring electrode by reducing the generated product with a limiting current. A computational scheme was developed to model this two electrode process. The disk electrode was operated through a current range from the limiting current to a zero net current. When operated at a zero net current, the disk can behave as a bipolar electrode with a non-zero

normal component of the current across the surface of the disk, except at the position where the current changes direction. The reaction is driven by the potential distribution over the disk generated by the ring limiting current. This calculation quantitatively explained anomalous diffusion coefficients measured at ring electrodes in ring-disk systems.

15. MEASUREMENT OF MASS TRANSFER RATES IN TURBULENT AND TRANSITION FLOW AT RING ELECTRODES

Peter Pierini and John Newman

A ring electrode was chosen to continue a study of mass transfer to a disk in transition flow so the active electrode could be placed in the desired flow regime. At high rotation speeds the flow varies from laminar at the center to turbulent at the edge of a disk, a situation which complicated the analysis of the data. A ring electrode was designed along with a complementing thermostated nickel cell. Data is currently being collected with the system.

16. SIMULTANEOUS REACTIONS AT DISK AND POROUS ELECTRODES*

John Newman

Advances in electrochemical engineering are reviewed, and the methodology of the analysis of electrochemical systems is outlined. Examples illustrative of current research concern simultaneous reactions for flow-through porous electrodes and the more fundamental system of a rotating-disk electrode. Here the undesirable side reaction is the formation of dissolved hydrogen, and the main reaction is the deposition of copper from sulfuric acid solutions. Distributions of reaction rate, concentration, and potential describe the detailed system behavior. The side reaction is responsible for the poorly defined limiting-current plateau on the disk electrode and provides a limit for the maximum flow rate at which good recovery can be achieved with the porous electrode.

* Plenary lecture presented at the 27th Meeting of the International Society of Electrochemistry, Zurich, Switzerland, September 6, 1976. (LBL-5757, November 1976, to be published in *Electrochimica Acta*.)

17. RESEARCH PLANS FOR CALENDAR YEAR 1977

John Newman

The fluid flow near the center of a rotating sphere will be investigated numerically. An iron rotating disk under passivation kinetics will be analyzed. The periodically constricted tube model of a packed bed will be further investigated. A high pressure electrochemical porous

bed reactor will be used to study dilute metal recovery.

18. 1976 PUBLICATIONS AND REPORTS

John Newman and Associates

Journals

1. P. Pierini, P. Appel, and J. Newman, Current Distribution on a Disk Electrode for Redox Reactions, *J. Electrochem. Soc.* 123 366 (1976).
2. R. White, C. M. Mohr, Jr., and J. Newman, The Fluid Motion Due to a Rotating Disk, *J. Electrochem. Soc.* 123, 383 (1976).
3. J. J. Miksis, Jr. and J. Newman, Primary Resistances for Ring-Disk Electrodes, *J. Electrochem. Soc.* 123, 1030 (1976).
4. M. Douglas LeVan and J. Newman, The Effect of Surfactant on the Terminal and Interfacial Velocities of a Bubble or Drop, *AIChE J.* 22, 695 (1976).
5. H. Gu and J. Newman, and D. N. Bennion, Analysis of Porous Electrodes with Sparingly Soluble Reactants, III. Short Time Transients, *J. Electrochem. Soc.* 123, 1364 (1976).
6. W. H. Smyrl and J. Newman, Current and Potential Distributions in Plating Corrosion Systems, *J. Electrochem. Soc.* 123, 1423 (1976).
7. K. W. Choi, J. Newman, and D. N. Bennion, Engineering Analysis of Shape Change in Zinc Secondary Electrodes, I. Theoretical, *J. Electrochem. Soc.* 123, 1616 (1976).
8. K. W. Choi, D. Hamby, J. Newman and D. N. Bennion, Engineering Analysis of Shape Change in Zinc Secondary Electrodes, II. Experimental, *J. Electrochem. Soc.* 123, 1628 (1976).
9. C. M. Mohr, Jr. and J. Newman, Mass Transfer to a Rotating Disk in Transition Flow, *J. Electrochem. Soc.* 123, 1687 (1976).

Papers Presented

1. W. H. Smyrl and J. Newman, Current Distribution on Electrodes at High Current Densities, Symposium on Engineering Analysis and Scale-up of Electrochemical Systems at the Washington meeting of the Electrochemical Society, May 5, 1976.
2. J. Newman, Simultaneous Reactions at Disk and Porous Electrodes. Plenary lecture at the Zurich meeting of the International Society of Electrochemistry, September 6, 1976.
3. J. Newman, F. DeSuaio and William Tiedemann (who presented the paper), Potential Distribution in Battery Grids, Tenth International Power Sources Symposium, Brighton, Sussex, England, September, 1976.
4. J. Newman, Flooded Porous Electrodes. Invited address before the Symposium on Porous Electrodes,

Theory and Practice, at the Las Vegas meeting of the Electrochemical Society, October 20, 1976.

5. R. White, J. A. Trainham, J. Newman, and T. W. Chapman (White presenting the paper), Potential-Selective Deposition of Copper from Solutions Containing Iron and Complexed with Chloride, Symposium on Selective Plating at the Las Vegas meeting of the Electrochemical Society, October 19, 1976.

6. J. Newman and J. A. Trainham (who presented the paper), A Porous Flow-Through Electrode Model: Application to Metal-Ion Removal from Dilute Streams. Symposium on Porous Electrodes, Theory and Practice, at the Las Vegas meeting of the Electrochemical Society, October 21, 1976.

7. J. Newman and P. Fedkiw (who presented the paper), Mass Transfer in a Deep Bed Porous Electrode Operating at the Limiting Current. Symposium on Porous Electrodes, Theory, and Practice, at the Las Vegas meeting of the Electrochemical Society, October 21, 1976.

8. J. Newman and P. Pierini (who presented the paper), Ring-Disk Electrodes. Symposium on High Current Density Electrode Processes at the Las Vegas meeting of the Electrochemical Society, October 21, 1976.

LBL Reports

1. W. H. Smyrl and J. Newman, Current and Potential Distributions in Plating Corrosion Systems, LBL-4999, February 1976.

2. W. Tiedemann and J. Newman, Flow-Through Porous Electrodes, LBL-4942, March 1976.

3. R. White, J. Trainham, T. Chapman, and J. Newman, Potential-Selective Deposition of Copper from Solutions Containing Iron and Complexed with Chloride, LBL-4986, April 1976.

4. C. Mohr and J. Newman, Mass Transfer in Turbulent Flow between Rotating Cylinders with Small Separation Gaps, LBL-5136, May 1976.

5. J. Trainham and J. Newman, The Minimum Concentration Attainable in a Porous Flow-through Electrode Reactor, LBL-5171, June 1976.

6. P. Fedkiw and J. Newman, Simulation of a Packed Bed as an Array of Periodically Constricted Tubes I: Creeping Flow, LBL-5199, July 1976.

7. P. Fedkiw and J. Newman, Simulation of a Packed Bed as an Array of Periodically Constricted Tubes II: Developed Mass Transfer at High Peclet Number in Creeping Flow, LBL-5406, July 1976.

8. P. Appel, Electrochemical Systems: Impedence of a Rotating Disk and Mass Transfer in Packed Beds, (Ph.D. thesis), LBL-5132, May 1976.

9. P. Pierini and J. Newman, Current Distribution on a Rotating Rising-Disk Electrode Below the Limiting Current, LBL-5492, August 1976.

10. J. Newman, Simultaneous Reactions at Disk and Porous Electrodes, LBL-5757, November 1976.

d. High Energy Oxidizers and Delocalized-Electron Solids

Neil Bartlett, Principal Investigator

1. GRAPHITE AND BORON NITRIDE SALTS

Richard Biagioni, Barry McQuillan and Neil Bartlett

Investigations last year established that the oxidizer $S_2O_6F_2$ was able to spontaneously oxidize graphite and boron nitride at room temperature to yield new intercalate salts, the boron nitride compound being the first example of a boron nitride analogue of the large class of graphite salts. We have attempted to define these materials better and this work is described under (a). Our efforts to make thermally and hydrolytically more stable new compounds in these classes are described under (b).

a. Graphite and Boron Nitride - $S_2O_6F_2$ Studies.

A routine two step preparation of $S_2O_6F_2$ on a 10-20 gram scale has been worked out using the XeF_2 , HSO_3F synthesis:

Powdered graphite and powdered boron nitride each incorporate SO_3F^- , from the $S_2O_6F_2$ reagent, within an hour at room temperature. The graphite salt has the composition $C_{12}SO_3F$ and is a first stage compound with an interplanar spacing of (C_0) 7.9 Å. In a vacuum this material loses $S_2O_6F_2$ and precession photographs indicate a new cell with $C_0 = 11$ Å. The x-ray diffraction data are consistent with this being a second stage compound (in which every other gallery of the graphite is occupied by SO_3F^-). A single crystal of natural graphite, supported in fine quartz wool in a quartz x-ray capillary, was characterized prior to immersion in $S_2O_6F_2$. Following intercalation, no evidence for ordering of the SO_3F^- placement was obtained, although the C_0 axis remained well-defined. Slower gas-phase intercalation may yield a more ordered structure. Microwave energy loss measurements, carried out on other single crystals both before and after intercalation, in collaboration with Professor A. Portis and Puan Ong (of the U.C. Berkeley Physics Dept.) show the salt to be a good electrical conductor but precise conductivities from this method lie in the future. Graphite samples with gold leads soldered in place, and housed in Pyrex tubes, have been supplied by Professor J. E. Fischer and Dr. T. Thompson of the University of Pennsylvania but none of these samples has so far survived the intercalation process. Reflectance spectroscopic studies on intercalated x-ray monochromator-grade graphite are in hand.

X-ray powder photographs of the blue, fully intercalated boron nitride, of approximate composition $(BN)_6SO_3F$, show that it is structurally akin to $C_{12}SO_3F$ and evidently a first stage material with $C_0 = 8.0$ Å. A resistivity measurement made by Puan Ong using the microwave

loss technique indicates that the salt is at least as good an electrical conductor as graphite. This places the behavior of the salt in sharp contrast with its parent, since boron nitride is an electrical insulator. Unfortunately large sheets of boron nitride do not intercalate SO_3F^- readily. Chips of pyrolytic boron nitride of ~3 mm cube edge, produced an irregular multi-sandwich of blue and white layers indicating haphazard intercalation. The same material, when powdered, gave a homogeneous product (as indicated by x-ray powder photography). Absence of general hkl reflections again indicates structural disorder in the SO_3F placement or the layer-layer relationship, or both.

(b) Thermally and Hydrolytically Stable Compounds. Since the hexafluorarsenate anion, AsF_6^- , has marked kinetic stability (its alkali salts can be recrystallized from water) and is yet able to stabilize unusually high oxidation states (as in the case of the dioxygenyl salt $O_2^+AsF_6^-$), it appeared to be an excellent candidate for the generation and stabilization of positive-carbon graphite salts. The salt $O_2^+AsF_6^-$ is easily preparable¹ and appeared to be ideal for graphite oxidation. A solvent has been found in sulfonyl chloride fluoride SO_2ClF . Graphite is oxidized at ~ -75° by a suspension of $O_2^+AsF_6^-$ in SO_2ClF . The characteristic blue color for graphite salts signals intercalation. A first stage material of composition $C_{10.8}AsF_6$ has been obtained for which an interlayer spacing of ~ 8 Å is indicated, but it is probable that even more AsF_6^- can be incorporated than is indicated by this formula. $C_{10.8}AsF_6$ is deep blue and appears to have greater hydrolytic stability than $C_{12}SO_3F$. Efforts will also be made to incorporate AsF_6^- into BN.

The powerfully oxidizing metal hexafluorides are also excellent agents for graphite salt generation and the noble metal hexafluorides in particular give promise of generating novel two-dimensional metals. (The noble metal hexafluoride graphite salts also provide the possibility, following reduction, for the dispersion of the noble metal in a graphite matrix).

We have found that graphite will not intercalate WF_6 at ordinary temperature but it will take up OsF_6 from a solution of OsF_6 in WF_6 . The deep blue to purple first stage compound, which gravimetry shows has the composition, $C_{7.2}OsF_6$, retains OsF_6 tenaciously and has a layer spacing of ~ 8.1 Å. This dimension is consistent with intercalation of OsF_6^- .

Boron nitride is oxidized by OsF_6 to yield BF_3 , N_2 and other fluorinated boron-nitrogen products, the OsF_6 being reduced simultaneously to OsF_5 .

1. J. Shamir and J. Binenboyin, Dioxygenyl Salts, Inorganic Syntheses XIV, 39 (1973).

2. SALTS OF AROMATIC CATIONS

Francis Tanzella and Neil Bartlett

Two years ago we succeeded in preparing the aromatic cation salts $C_6F_6^+AsF_6^-$ and $C_{10}F_8^+AsF_6^-$. Efforts were made at that time to prepare the analogous salt of the simplest and best known of the aromatics, benzene. There were indications that such a salt had been prepared, in very low yield, by interaction of benzene with the perfluorobenzene cation salt:

the low yield probably being due to accompanying decomposition of the $C_6F_6^+AsF_6^-$ (which is thermodynamically unstable). Since the $C_6F_6^+AsF_6^-$ synthesis was itself cumbersome, we set out to find an improved preparation for it. Simultaneously an independent route to $C_6H_6^+$ salts was also sought.

a. A New Preparation of $C_6F_6^+AsF_6^-$. In the original synthesis of $C_6F_6^+AsF_6^-$ the oxidant $O_2^+AsF_6^-$ had been brought into contact with C_6F_6 in tungsten hexafluoride as solvent. The solvent, although inert to oxidation and of fair heat capacity is nevertheless rather high melting (2.5°) and is not a commonly available reagent. We have found that SO_2ClF (m.p. -124.7° ; b.p. 7.2°) is a solvent for both C_6F_6 and $O_2^+AsF_6^-$ and as a consequence of its low melting point the interaction can be brought about at lower temperatures and under greater control. Yields of $C_6F_6^+AsF_6^-$, based on $O_2^+AsF_6^-$, greater than 70% are now routine in multigram quantities.

b. Oxidation of Benzene, Napthalene, Anthracene, and Phenanthrene. With the finding that SO_2ClF is a solvent for $O_2^+AsF_6^-$ it appeared possible that it could serve as the solvent for $C_6H_6^+AsF_6^-$ salt synthesis. Indeed the low melting point (m.p. -124.7°) of SO_2ClF suggested that controlled oxidation of C_6H_6 using $O_2^+AsF_6^-$ itself might be possible and this has proved to be so. Approximately quantitative elimination of O_2 from $O_2^+AsF_6^-$ occurs at $\sim -100^\circ$ when the benzene solution in SO_2ClF makes contact with it. The resulting solid appears black in bulk but thin crystallites are orange-red by transmitted light. Analysis for C and H have indicated that the solid is $C_6H_6AsF_6$, contaminated slightly with benzene, but greater control in the synthesis will probably yield analytically pure material.

Analogous reactions with $O_2^+AsF_6^-$ have been carried out using naphthalene, anthracene, and phenanthrene in place of C_6H_6 . The products are all either dark blue or very dark green and evidently contained oxidized aromatic species. We have no structural or magnetic data yet to discern between simple salt or polymeric cation species in these materials.

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3. EVIDENCE FOR Cl_2^+ SALTS

Neil Bartlett, Lionell Graham, and Warren E. Falconer

We have long known¹ that iridium hexafluoride gas interacts with chlorine gas in 1:1 stoichiometry to generate a yellow solid, which, at room temperature, decomposes to yield iridium pentafluoride. Infrared studies carried out on the 1:1 solid deposited on a silver chloride window at <12 K have now established that it is a hexafluoroiridate(V). The compound is associated with a single sharp symmetrical absorption at 635 cm^{-1} characteristic of ν_3 for IrF_6^- . It is therefore highly probable that the salt is $Cl_2^+IrF_6^-$. The small-particle nature of the solid has frustrated attempts to obtain Raman spectra from this material, but since the solid is stable indefinitely at -75° there is the prospect of being able to develop particle growth in a suitable solvent at or below this temperature. Chlorine is also oxidized by PtF_6 but, at room temperature, chlorine fluorides result. At low temperatures, however, the interaction is again simple, the sole infrared absorption (in the range $4000\text{-}400\text{ cm}^{-1}$) being at 630 cm^{-1} and characteristic of ν_3 PtF_6^- . This again indicates that the chlorine compound is a dichlorinyl compound, $Cl_2^+PtF_6^-$.

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4. RESEARCH PLANS FOR CALENDAR YEAR 1977

Neil Bartlett

a. Delocalized-Electron Solids Involving Cationic Rings Chains and Sheets. Studies of oxidized graphite and boron nitride will continue but there will be a major effort to synthesize other hydrocarbon cation salts. If the aromatic hydrocarbon cations do indeed polymerize and produce one- or two-dimensional electrical conductors then a very large variety of conductors will be synthesizable. Aromatic rings linked to one another (as in di and triphenyl) and aromatic rings linked by chains will provide for cross linking of the polymers. Certainly much effort will be placed in the development of crystals of $C_6H_6AsF_6$ and any new compounds. Electrical magnetic and spectroscopic studies will aim to define these materials as well as possible.

b. Electrochemistry Involving High-Energy-Oxidizer Components. The electrolysis of HSO_3F , using graphite and graphite salt electrodes will be further pursued in order both, to find the best conditions for synthesis of $S_2O_6F_2$ (an example of a high oxidation-state material) and to observe the effectiveness of graphite fluorosulfate as an anode. Electrolysis of melts such as $XeF_5^+RuF_6^-$ would be tried subsequent to experience with the fluorosulfuric acid system.

c. The Nature of Fluorine-Bridge Bonding. Superexchange interactions in transition metal fluorides are often important in controlling the magnetic properties of the fluorides but the superexchange is tied to structural features. Thus the rutile type difluorides are antiferromagnetic as are the structurally related tetrafluorides of Ir, Pt, Pd and Rh. In these fluorides the bridging angles M-F-M are $\sim 130^\circ$. It is known from the pentafluoride structures² that the M-F-M bridge angles decrease from left to right in each row in the periodic table and much the same is expected for the low fluorides, but tetrafluorides of W, Re, Os, Tc, Rn are either unknown or are poorly characterized. In the known pentafluorides and trifluorides of these elements the coordination of the metal atom in fluorine is six (octahedral). The stoichiometry therefore will require two kinds of F ligand in a tetrafluoride, one bridging and the other unique. This can produce a sheet type structure (with the unique F ligands above and below the bridging F atoms in the plane of the sheet) or a truly three dimensional structure as in the IrF_4 type compounds. It is difficult to forecast which type will be adopted by WF_4 etc., and it is also difficult (even with structural knowledge) to predict the magnetic behavior. Synthetic, structural, and magnetic studies would be pursued in concert.

d. A Search for Novel $\pi^*-\pi^*$ Lewis Acid-Base Cations. Recent work has indicated that the O_2^+ cation can act as a Lewis acid to generate an $(\text{O}_2\text{B})^+$ complex cation. Thus chlorine interacts with colorless O_2^+ salts to yield purple solids from which the chlorine can be retrieved under reduced pressure. Orbital symmetry suggests that the $(\text{Cl}_2\text{O}_2)^+$ adduct could be a cyclic species or a chain species in which the Cl_2 is a π^* donor and the O_2^+ a π^* acceptor. We will endeavor to establish the Cl_2O_2^+ species and investigate the possibility of similar species in the $\text{NO}^+/\text{nitric oxide}$ system providing a template species for the conversion of NO to N_2 and O_2 .

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Neil Bartlett and Associates

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1. N. Bartlett, "Oxidative Fluorination", at Symposium on Introduction of Fluorine into Organic and Inorganic Compounds, Centennial A.C.S. Meeting, April 5-8, N.Y., 1976.
2. N. Bartlett, "From O_2^+ Salts to Synthetic Metals" in Frontiers in Chemistry Series at Wayne State University, May 17, 1976.
3. N. Bartlett, "Noble-Gas Chemistry" at the University of Bordeaux, Bordeaux, France, July 13, 1976.
4. N. Bartlett, "The Characterization of Novel Oxidation States" in the Symposium on The Physical Characterization of Fluoride Materials at the 172nd A.C.S. National Meeting, San Francisco, August 30 - Sept. 3, 1976.
5. N. Bartlett, "The Fluorine Ligand" in the Symposium on The Unique Role of Fluorine in the Teaching of Chemistry at the 172nd A.C.S. National Meeting, San Francisco, August 30 - Sept. 3, 1976.

e. Conversion of Coal to Clean Liquid and Gaseous Fuels

Gabor A. Somorjai and Alexis T. Bell, Principal Investigators

1. THE HYDROGENATION OF CO AND CO₂ OVER POLY-CRYSTALLINE RHODIUM: CORRELATION OF SURFACE COMPOSITION, KINETICS AND PRODUCT DISTRIBUTIONS

B. A. Sexton and G. A. Somorjai

Rhodium, in the form of a small surface area ($\sim 1 \text{ cm}^2$) polycrystalline foil was used to study the CO-H₂ and CO₂-H₂ reactions at low ($\sim 10^{-4}$ Torr) and at high (700 Torr) pressures in the same apparatus. Reaction rates and product distributions were monitored with a mass spectrometer and a gas chromatograph, respectively, and the surface composition was determined by Auger electron spectroscopy. The various binding states of CO were studied by thermal desorption. Under reaction conditions (250 to 350°C, 700 Torr), the surface is covered with a catalytically active carbonaceous deposit while some oxygen is located below the surface. No surface oxygen was detectable after reaction as the removal of chemisorbed species by either the CO-O₂ or H₂-O₂ reactions was rapid at low temperatures. Carbon monoxide was found to adsorb in molecular form on clean Rh surfaces, but dissociated on surfaces pretreated in CO, or by heating in the presence of gaseous CO. Co-adsorption of H₂/CO mixtures at low pressures increased the amount of molecular CO but no changes in CO binding energy were observed.

At low pressures (10^{-4} Torr) the reaction probability for both the CO-H₂ and CO₂-H₂ reactions is too low to detect products. At high pressures (700 Torr), the rates, activation energy (24 ± 3 kcal) and product distributions from the small surface area Rh foil is nearly identical to that obtained on a dispersed rhodium catalyst. The CO₂-H₂ reaction produces methane exclusively and with a lower activation energy (16 ± 2 kcal) than for the CO-H₂ reaction. Pretreatment of the clean surface changes the product distribution and the rates in both reactions. Pretreatment with acetylene deposits surface carbon and facilitates chain growth in the CO-H₂ reaction (a higher percentage of C₂ and C₃ products). Pretreating with oxygen dissolves oxygen in the bulk and increases the methanation rate by up to a factor of five over the clean surface. It appears that active rhodium-carbon-oxygen complexes form at the surface and rehydrogenate to yield the various products.

2. STUDIES OF HYDROCARBON SYNTHESIS

a. Adsorption and Desorption of CO and H₂

Wayne A. Bollinger and Alexis T. Bell

The adsorption of H₂ and CO on a silica-supported Ru catalyst was studied as part of a program related to the synthesis of hydrocarbons.

Hydrogen adsorption was found to be slow and followed Elovich kinetics for temperatures between 20 and 250°C. The adsorption isotherms were composed of two parts characterized by reversible and irreversible adsorption. The nature of the irreversibly adsorbed H₂ was studied by thermal desorption. The TD spectra showed five peaks located at 85, 140, 200, 280, and 310°C. The two low-temperature peaks are believed to be H₂ adsorbed as the molecule whereas the three high temperature peaks correspond to atomically adsorbed H₂.

Carbon monoxide adsorption was considerably more rapid than H₂ and precluded accurate measurement of kinetics. As in the case of H₂, a part of the adsorbed CO is held reversibly and part irreversibly. Thermal desorption shows that CO is adsorbed in at least three different forms. Prolonged exposure of the catalyst to CO was found to reduce the catalyst capacity for H₂ adsorption. However, H₂ adsorption capacity was restored following oxidation and reduction of the catalyst. These results suggest that H₂ adsorption was inhibited by carbon on the Ru surface, formed by dissociation of CO.

b. Simultaneous Investigation by IR Spectroscopy and Kinetic Analysis of Hydrocarbon Synthesis from CO and H₂

John Ekerdt, Steve Kellner, and Alexis T. Bell

Construction has been completed of an apparatus for performing IR studies under reaction conditions. The central part of the apparatus is a small volume cell which contains the catalyst. Two cell designs have been evolved, the first suited for operation at pressures between 10^{-4} and 10^3 Torr and the second for pressures between 10^3 Torr and 10^5 Torr. Product gas analysis is performed by mass spectrometry. The apparatus will be used to study the kinetics and mechanisms of hydrocarbon synthesis over supported Ru, Fe, and Co catalysts.

c. Thermal Desorption Spectroscopy Applied to the Study of CO and H₂ Adsorption on Supported Metal Catalysts.

Gordon Low, Minoru Uchida, and Alexis T. Bell

A thermal desorption spectrometer has been designed and is being assembled. Detection of species desorbed from silica or alumina supported catalysts is accomplished by mass spectrometry. By using a low thermal mass cell and low catalyst concentrations, heating rates of 1 to 5 K/sec will be achieved. Very rapid heating is desired to minimize interconversion between adstates during desorption. This apparatus will be used to obtain binding energies and surface concentration of different adspecies produced by adsorption of CO and H₂. Experiments will also be conducted to identify which adspecies participate in catalysis.

3. CATALYZED GASIFICATION OF COAL CHAR

Michael J. Veraa and Alexis T. Bell

Aqueously impregnated K_2CO_3 is found to be a significantly more active catalyst for the steam gasification of coal char than the alkali metal chlorides. At a constant metal cation loading the latter catalysts are found to behave similarly, causing a retardation in the gasification rate until about 80% of the fixed carbon has been gasified (see Fig. 1). Experiments conducted with

Fig. 1. Effect of different catalysts on the steam gasification of coal char: catalyst loading = 5.1×10^{-4} gm atom metal cation/gm coal. (XBL 764-5424)

KOH gave results identical to those obtained with K_2CO_3 . This observation is attributable to the conversion of KOH to K_2CO_3 during the charring procedure. The superior catalytic activity of K_2CO_3 can possibly be explained in terms of the following sequence of steps

Experiments were performed to determine the effects of K_2CO_3 loading and gasification tempera-

ture on the rate of gasification and product gas composition. The results show that gasification is enhanced with increasing K_2CO_3 loading and reaction temperature. Increasing K_2CO_3 loading causes CO to be formed in preference to CO_2 and H_2 and suppresses the formation of CH_4 . Increasing temperature also causes CO to be formed in preference to CO_2 and H_2 but enhances the production of CH_4 . These trends can be interpreted in terms of a simple mechanism of char gasification.

Table 1. IR band assignments.

Adsorbate	State of Ru surface	$\nu(\text{cm}^{-1})$	Surface structure
NO	oxidized	1810	Ru-NO^+
NO	oxidized	1860-1880	Ru^+-NO^+
CO	reduced	2040	Ru-CO
CO	oxidized	2130, 2070	Ru^+ CO

4. TRANSITION METAL CLUSTER CATALYSIS IN HYDROGENATION AND HYDROGENOLYSIS

A. J. Barkovich, D. K. Mitchell, P. Perkins, and K. P. C. Vollhardt

Novel organic ligands are being constructed that might serve as matrices for transition metal cluster formation to be used in catalytic hydrogenation and potential hydrogenolysis of benzenoid aromatic systems. They involve compounds containing multiple coordination sites to which metals might be attached in a sequential fashion.

Reaction of tribromide **1** with $\text{NaCo[P(OMe)}_3\text{]}_4$ gave two η^5 -allyl cobalt complexes the structure of one of which appears to be **2**. This compound effects the conversion of benzene to cyclohexane under homogeneous conditions. Similarly model compound **3** acts as an efficient benzene hydrogenation catalyst. The interconversion of compounds of the type **2** to trinuclear cluster **4** is currently being investigated. In addition comparative data of catalytic activity are being assembled in an effort to determine the possible presence of cluster template effects.

The synthesis of 1,5,9-cyclododecatriyne **5**, a unique potential ligand, has been achieved via classic routes. It reacts with $\text{Co}_2(\text{CO})_8$ and $\text{CpCo}(\text{CO})_2$ to give organometallic complexes in which **5** retains its structural features. Thermally, **5** cyclizes to tricyclobutabenzene **6** which can be trapped with dimethylmaleate to give the triadduct **8**. In the absence of trapping agent **6** is converted to hexaradialene **7**, an extremely

reactive and air sensitive hydrocarbon. Calculations using group equivalent techniques predict the $\underline{5} \rightarrow \underline{6}$ interconversion to be exothermic by at least 23 kcal. The formation of $\underline{7}$ in the pyrolysis of $\underline{5}$ is explained by the decreased aromatic character of potential cyclohexatriene $\underline{6}$ ($\Delta H_f > 10$ kcal/mol) which renders the $\underline{6} \rightarrow \underline{7}$ reaction exothermic.

Two polymer supported cyclopentadienyl cobalt carbonyl syntheses have been developed as shown in the scheme. The resins employed consisted of

Scheme

chloromethylated polystyrene--1% divinylbenzene (Bio-Rad Bio Beads SX-1) and 3% cross-linked macroreticular polystyrene-divinylbenzene copolymer. Heating or irradiation (Hanovia medium pressure Hg-lamp) generates highly reactive, coordinatively unsaturated cobalt monocarbonyls under pseudodilution or "hyper-entropic efficacy" conditions. However, chain

mobility is sufficient to rapidly lead to resin immobilized dinuclear di- and tricarbonyl clusters. Further heating or exposure to light effects complete (but reversible) carbon monoxide removal to give deep green polymers the catalytic activity of which is under investigation.

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5. ACTIVATED BENZENOID HYDROCARBONS*

R. L. Hillard and K. P. C. Vollhardt

The chemistry of coal is largely governed by the reactivity of its component molecules. These consist of aromatic, hydroaromatic, heterocyclic and partially saturated molecular subunits. In an effort to gain some understanding of the electronic structure of coal, the chemistry of its sub-moieties, the mechanisms of its hydrogenation and hydrogenolysis in the presence of hydrogen, and the potential carcinogenicity of its component hydrocarbons, several activated model benzenoid aromatic structures have been synthesized. Their physical and chemical properties answer some intriguing questions concerning the nature of benzene aromaticity and activation of aromatic polycycles by fusion to strained rings. For example, 4,5-bromiodobenzocyclobutene $\underline{1}$ serves to generate cyclobuta[1,2-d]benzene $\underline{2}$ by treatment with butyl lithium or magnesium. Trapping with furan results in cycloadduct $\underline{3}$, while in the absence of a trapping

agent dimerization and (formal) trimerization occur to 2,3:6,7-dicyclobutabiphenylene $\underline{4}$ and 2,3:6,7:10,11-tricyclobutatriphenylene $\underline{5}$, respectively. Compound $\underline{4}$ is one of the most strained benzenoid hydrocarbons known and as such exhibits remarkable reactivity. It is air-sensitive and hydrogenates instantly at normal pressures and room temperature to the totally saturated $\underline{6}$. Cycloaddition of dienophiles occurs to both "external" four rings. Comparison of the spectral (see, for example, Fig. 1) and chemical data on $\underline{4}$ with other less strained model systems (e.g., $\underline{8}$, $\underline{9}$) shows a clear gradation of strain along the series. It should be noted that biphenylene is a component of coal.

Fig. 1. Electronic spectra of hydrocarbons 4, 8 and 9 in 95% alcohol. (XBL 772-7796)

From concentrated solutions of **2** the triphenylene **5** can be isolated. This compound is the first polycyclic benzenoid to be synthesized that is fused to three activating strained rings and its properties in comparison with model **10** and triphenylene itself reflect the added degree of activation. Again hydrogenation is extremely facile, leading to **7**, in striking contrast with triphenylene which requires high pressure and heat before hydrogen uptake occurs. The electronic spectra along the series exhibit bathochromic shifts consistent with the simple strain model that accounts for the relative reactivity of these compounds (Fig. 2). Polycycles **5** and **10** were tested for mutagenic activity ("Ames test" on *Salmonella typhimurium*) and found to be inactive.

Finally, the current "world record" in strained benzene chemistry, 1,2-cyclopropa-4, 5-cyclobutabenzene **12**, is also accessible via the synthesis of benzocyclobutene **11** followed by bromination and elimination. Despite the extraordinary

strain present in **12** there seems to be a large degree of aromatic character left as judged by the NMR criterion: the unsaturated protons in the aromatic region, τ 3.15. On the other hand the longest wavelength electronic absorption (λ_{max} 294 nm) is the most blue-shifted yet observed for a simple tetraalkylated benzene. The relative stability of **12** should serve as an incentive in the search for other more highly distorted analogs.

Fig. 2. Electronic spectra of triphenylene, cyclobutatriphenylene **10** and tricyclobutatriphenylene **5** in 95% ethanol. (XBL 772-7795)

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6. LIGAND ACTIVATION BY TRANSITION METAL COMPLEXATION

W. G. L. Aalbersberg and K. P. C. Vollhardt

Coal is a polymeric substance, composed of two and three dimensional fused-ring aromatic-hydroaromatic structures with covalent bonding, accompanied by significant hydrogen bonding and π -electron association. Bridges between the fused moieties consist of carbon chains, sometimes incorporating oxygen and sulfur. Hydrogenolysis by transition metal catalyzed processes will lead via intermediates or transition states of carbenium ion, radical or carbanion character (depending on catalyst and substrate) to soluble and volatile molecules of reduced size. These intermediates will be affected in their stability by adjacent aromatic centers, which in turn will be affected by complexation to metals. This suggests the intriguing possibility of "co-catalysis" in which certain bonds to be cleaved are activated (Fig. 1) by interactions with metal complexed aromatic centers through bond and/or through space, but in which the actual cleavage reaction is catalyzed by a second, possibly different metal catalyst. To test for this effect we have prepared various derivatives of iron tricarbonyl complexed bicyclo[4.2.1]nonatrienyl systems **1** in which reactions at a center spatially removed from the complexing iron can be observed and compared with the uncomplexed case. Treatment of bicyclo[4.2.1]nona-2,4,7,9-trienone with $\text{Fe}_2(\text{CO})_9$ gave yellow,

Fig. 1. Possible activation of certain bonds in coal by transition metal complexation.
(XBL 772-7794)

crystalline complex **2**. This compound is exceedingly unreactive towards hydride reducing agents when compared with the free ligands, an unexpected result of complexation. Reduction was achieved

with lithium aluminum hydride (-75°C) to alcohol **3**, exhibiting the same stereochemistry as the alcohol obtained by kinetic reduction of the free bicyclic trienone. Reduction of **2** with diimide gave **4** which was reduced readily with hydride to give **5**. The rates of solvolysis of the tosylates derived from **3** and **5** should give some quantitative estimate of the relative amount of backbonding that occurs in these complexes. ^1H and ^{13}C -NMR data have been compiled on **2**, **4** and their respective ligands. The observed chemical shifts are not compatible with homo-aromaticity and bicycloaromaticity effects proposed earlier to be operative in bicyclo[4.2.1] nonatrienone.

7. THE NATURE OF SO FROM THIIRANE OXIDES*

W. G. L. Aalbersberg and K. P. C. Vollhardt

Sulfur monoxide is an interesting sulfur analog of oxygen and is a possible intermediate in the

production of polluting higher sulfur oxides from combustion and incineration of high sulfur containing coal. Little is known about its organic chemistry and the nature of its electronic states in its reactions.

The mechanism of the thermal decomposition of thiirane oxides, potentially valuable sources of sulfur monoxide in solution, has been a matter of considerable controversy. Unimolecular decomposition of the parent thiirane oxide ($E_a \approx 35 \text{ kcal/mol}$) is expected to result in the "spin-allowed" formation of both singlet ethylene and sulfur monoxide, the latter being an excited state species quite possibly accessible thermodynamically. However, attempts to detect singlet sulfur monoxide by physical (microwave, EPR) or chemical means (trapping with dienes and trienes, respectively) have provided evidence best accommodated by the assumption of the intermediacy of the corresponding ground state triplet species. Similarly, decomposition of stereochemically labeled thiirane oxides (*cis* and *trans* diphenyl-, or dimethylthiirane oxide) resulting in ethylene products in which stereochemical integrity has been lost have been interpreted as processes in which sequential carbon-sulfur bond breaking proceeds via a diradical intermediate.

We have prepared the simplest stereochemically labeled thiirane oxides, *cis* and *trans*-dideuteriothiirane oxide (**1a,b**) via the stereospecific formation of the corresponding deuterated epoxides and thiiranes (Scheme), and have obtained

the stereochemical results of their decomposition both in the gas and solution phase. Deuterium decoupled ^1H -NMR spectra of **1a** and **1b** are shown in Fig. 1. The *trans*-isomer **1b** was contaminated with approximately 5% of the *cis*-compound.

Pyrolysis of **1** in the gas (vacuum transfer through a hot tube, $350^{\circ}\text{C}/0.05 \text{ mm}$) or solution phase (1,2,4-trichlorobenzene, 150°C) gave deuterated ethylenes with 95% retention of stereochemistry. Pyrolysis of **1** at lower temperatures led to partial recovery of starting material with unchanged stereochemistry. In order to shed some light on the origin of the 5% crossover product, undeuterated thiirane oxide was thermally decomposed in the presence of pure *trans*-dideuterioethylene (static system). No *cis*-dideuterioethylene was observed in this experiment.

Our results provide for the first time unambiguous evidence for the mode of decomposition of simple thiirane oxides. They indicate that these compounds are not unusual in their thermal behavior when compared with their higher and lower oxidized analogs and suggest analogous modes of extrusion of the sulfur-containing species. Our data reopen the question as to the nature of sulfur monoxide formed initially in thiirane oxide decompositions, a question that may ultimately only be answered by spectroscopic means. Although the observed (albeit small)

Fig. 1. Deuterium decoupled 100 MHz ^1H -NMR spectra of cis- and trans-dideuteriothiirane oxide 1a,b. (XBL 772-7797)

crossover in our experiments tends to point to a biradical mechanism involving production of ground state species, possibly involving a stereochemically rather rigid Π -thiacyclopropane oxide "biradical," a significant contribution of a concerted process cannot be ruled out at present.

* Partially supported by Research Corporation.

8. THE SYNTHESIS, CHARACTERIZATION AND EVALUATION OF SOLUABLE FISCHER-TROPSCH CATALYSTS

J. C. Smart, C. J. Curtis, B. L. Pinsky, and J. L. Robbins

The ready availability of H_2/CO mixtures from coal gasification and the water-gas shift reaction has made these molecules attractive starting materials for the synthesis of liquid hydrocarbons. At present there are no homogeneous catalysts

analogous to existing heterogeneous catalysts for methanol synthesis, methanation and Fischer-Tropsch synthesis of hydrocarbons. Recent work with reduced, soluble mononuclear transition metal compounds has demonstrated the stoichiometric transformation of coordinated carbon monoxide to oxidized metal formyl,¹ and alkoxy complexes.²

We have synthesized and characterized a variety of coordinatively unsaturated dinuclear complexes of the early transition metals in an effort to coordinate and activate both molecular hydrogen and carbon monoxide.³ These compounds were synthesized utilizing an *in situ* preparation of the bridging bicyclopentadienyl or fulvalene dianion ligand. Reaction with molybdenum acetate yields bis(fulvalene)dimolybdenum,⁴ which reacts with carbon monoxide to yield the complex shown in Fig. 1. This complex has a bridging carbonyl ligand, which is unprecedented in molybdenum chemistry, a metal-metal bond and two bridging fulvalene ligands. A related system

Fig. 1. The 360 Hz pmr spectrum of bis(fulvalene)-dimolybdenummonocarbonyl in 99% tetrahydrofuran- d_8 . The large peak marked *, and the shoulder at lower field are solvent resonances. (XBL 772-7793)

containing one bridging ligand, unsubstituted cyclopentadienyl ligands, two metal hydride moieties and a metal-metal bond has been synthesized. A series of neutral and cationic bis(fulvalene) divanadiumdicarbonyl complexes has also been prepared, and further studies in the titanium group metals are planned. Catalytic studies of these complexes are underway in an effort to add H_2 oxidatively to yield metal hydrides, followed by migratory insertion of coordinated CO to yield intermediate formyl complexes and ultimately methanol. Alternatively, CO insertion in concert with metal hydride reduction may provide a means of aliphatic chain growth and lead to higher molecular weight products.

Various structural and spectroscopic studies of group VIII metal complexes indicate that a bridging fulvalene ligand can propagate strong magnetic and electronic interactions.⁵ We are presently structurally modifying this ligand system and developing new ligands to bridge triangular and square arrays of metal atoms.

Such compounds will enable the role of the bridging ligand in catalytic processes to be

probed, and represent a connection between mononuclear metal complexes, larger metal clusters, and metal surfaces.

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9. RESEARCH PLANS FOR CALENDAR YEAR 1977

G. A. Somorjai and Alex T. Bell

The mechanism of selective formation of hydrocarbons from CO, CO₂ and H₂ on iron surfaces will be explored.

The kinetics of NO reduction by CO and H₂ will be investigated on supported Pt, Ru, and Rh catalysts. The results will be correlated with infrared investigations to establish reaction mechanisms and critical reaction steps which distinguish these catalysts.

Hydrocarbon synthesis on supported Ru, Rh, Fe, and Co catalysts will be investigated over a broad range of pressures. Parallel infrared studies will be used to identify the nature of reaction intermediates.

Thermal desorption spectroscopy will be used to determine the binding energies, surface coverages, and desorption kinetics of different adspecies produced by adsorption of NO, CO, and H₂ on supported metal catalysts. Correlations with infrared observations will be made to obtain extinction coefficients for adsorbed species.

Apparatus for the performance of transient response experiments will be developed so that gas and surface compositions can be monitored as functions of time following the imposition of a concentration disturbance in the gas phase. This technique will be used to study the correlation between infrared observable surface species and reaction kinetics.

We shall attempt to synthesize new transition metal cluster catalyst systems by the use of specifically constructed organic ligand templates. Their effectiveness in hydrogenation and hydrogenolysis of benzenoid aromatics, hydroaromatics, and coal will be explored.

The mechanism of catalytic hydrogenation of polycyclic benzenoid hydrocarbons will be studied on electronically activated substrates.

Pt-cluster complexes will be explored in potential ring opening reactions on benzenoid cycles.

The effect of remote transition metal complexation on catalytic hydrogenation and hydrogenolysis of reactive centers will be measured.

Polymer supported complexes will be utilized in catalytic chemistry, cluster synthesis, CO reduction with hydride reagents, and the CO/H₂ reaction to produce hydrocarbons.

10. 1976 PUBLICATIONS AND REPORTS

Gabor A. Somorjai, Alex T. Bell, and Associates

Journals

1. D. H. Lorimer and A. T. Bell, An Inexpensive Data Logging System, *I&EC Fund.* **15**, 71 (1976).
2. E. L. Force and A. T. Bell, The Effects of Dichloroethane Moderation on the Adsorbed Species Present during the Oxidation of Ethylene Over Silver, *J. Catal.* **44**, 175 (1976).
3. R. L. Funk and K. P. C. Vollhardt, 1,2-Dihydrocyclobuta[b]-triphenylene and 1,2:5,6:9,10-Hexahydrotriscyclobuta[b,h,n]-triphenylene, *Angew. Chem.* **88**, 63 (1976); *Angew. Chem. Intern. Edn.* **15**, 53 (1976).
4. A. J. Barkovich and K. P. C. Vollhardt, 1,5,9-Cyclododecatriyne. Synthesis and Conversion to Intermediate 1,2:3,4:5,6-Tricyclobutabenzene, *J. Am. Chem. Soc.* **98**, 2667 (1976).
5. R. L. Hillard III and K. P. C. Vollhardt, Cyclobuta[1,2-d]-benzynes. Generation, Trapping and Dimerization to 2,3:6,7-Dicyclobutabiphenylene, *J. Am. Chem. Soc.* **98**, 3579 (1976).
6. R. L. Funk and K. P. C. Vollhardt, 1,5-Hexadiyn-3-ol Ethers as Tetramethynyl Synthons in Cobalt Catalyzed Acetylene Cooligomerizations; A One Step Synthesis of 2,3,6,7-Tetrakis(trimethylsilyl)naphthalene, *J. C. S., Chem. Commun.*, 833 (1976).
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1. M. J. Verea, Coal Char Gasification Using Alkali Metal Catalysts, (M.S. thesis), LBL-4498, April 1976.
2. W. A. Bollinger, Gravimetric Adsorption of Hydrogen and Carbon Monoxide on a Supported Ruthenium Catalyst, (M.S. thesis), LBL-5207, May 1976.
3. M. J. Verea and A. T. Bell, The Effect of Alkali Metal Catalysts on the Gasification of Coal Char, LBL-5777, December 1976.
4. B. A. Sexton and G. A. Somorjai, The Hydrogenation of CO and CO₂ Over Polycrystalline Rhodium:

Correlation of Surface Composition, Kinetics and Product Distributions, LBL-5178, July 1976.

Papers Presented

1. A. T. Bell, Infrared Spectroscopy as a Tool in the Study of Catalyzed Reactions, Chemical Engineering Department, University of Delaware, Newark, Delaware, February 1976.
2. A. T. Bell, Infrared Spectroscopy as an Aid to Understanding the Catalytic Reduction of NO, Philadelphia Catalysis Club, Philadelphia, Penn., February 1976.
3. A. T. Bell, Applications of Infrared Spectroscopy in the Study of Catalytic Reactions, Surface Science and Catalysis Science Seminar, MMRD, LBL, Berkeley, Calif., October 1976.
4. A. T. Bell, An Infrared Study of the Interactions of NO, CO, and H₂ on Silica-Supported Ru, The California Catalysis Society, Los Angeles, Calif., November 1976.

Invited Lectures

1. University of California, Santa Cruz, Calif., January 21, 1976.
2. University of Southern California, Los Angeles, Calif., March 26, 1976.

3. International Business Machines, San Jose, Calif., May 10, 1976.

4. Massachusetts Institute of Technology, Cambridge, Mass, October 5, 1976.

5. University of California, Davis, Calif., October 12, 1976.

6. University of Oregon, Eugene, Oregon, October 19, 1976.

7. University of California, San Diego, Calif., December 3, 1976.

Meetings

1. 31st Annual Northwest Regional Meeting, American Chemical Society, Reno, Nevada, June 14-15, 1976.
2. Coal Chemistry Workshop, Stanford Research Institute, Palo Alto, Calif., August 26-27, 1976.
3. American Chemical Society Centennial Meeting, 172nd ACS National Meeting, San Francisco, Calif., August 29-September 3, 1976.
4. Colloque International du Centre National de Recherches Scientifiques, Saint-Raphaël, France, September 7-11, 1976

C. MOLECULAR AND ATOMIC SCIENCES

1. CHEMICAL PHYSICS

a. Energy Transfer Processes in Organic Solids

Charles B. Harris, Principal Investigator

1. INTRODUCTION

Charles B. Harris

In the past year our laboratory has been engaged in developing several new methods for investigating a variety of problems associated with energy transfer in solids and on surfaces. The first of these is of a technique for obtaining the spectra of the molecules absorbed on metal surfaces. Over the past year we have succeeded in building a ultra-high vacuum chamber for studying reflectance and emission spectroscopy of molecules absorbed on metal surfaces at low coverages. The instrument is capable of operating over a range of 4 K to 450 K maintaining a background pressure of better than 10^{-11} Torr. In addition it has associated with it the standard surface techniques of LEED, Auger and quadrupole mass spectra so that the results of the experiments can be correlated with the composition and structure of the organic adlayer. In addition, we have solved the coupled boundary value equations for determining the optimum geometry in the experiments and to assess what sort of signal-to-noise we can expect for various coverages of molecules having different oscillator strengths in their transitions. This project has involved a considerable amount of instrumentation which is now complete and in the final debugging stages.

The second area which we have been developing is the use of picosecond spectroscopy for studying energy transfer and relaxation processes in condensed phases and for studying electron-hole recombination rates of semiconductors. For these studies we have constructed a selected single pulse Nd laser having transform limited pulses of 5 psec. Preliminary results on vibrational energy transfer and relaxation in liquid and solid phases are presented in articles No. 6. The important questions to ascertain in condensed phase are whether or not energy transfer processes in solids at room temperature reflect the periodic potential of the solid or whether thermal motion gives rise to energy transfer processes similar to those in liquids. A secondary area in which we are applying picosecond spectroscopy is in the investigation of electron-hole recombination rates on semiconductor surfaces. The semiconductors of interest are those which catalyze the photo-electrolysis of water to oxygen and hydrogen. In these studies we have combined laser techniques with ellipsometry and have developed a technique for studying surface recombination.

Third area which has been developed in the past two years is the use of thermal modulation or heat pulse techniques for the investigation of energy transfer in molecular solids. These studies are presently in an advanced stage and have yielded a large variety of new and important observations ranging from the ability to determine kinetic parameters for energy transfer directly to the measurement of the heat capacity of solids via the risetime of emission from impurity states.

Finally we are continuing research in the area of energy transfer processes of molecular solids using the coherent spin resonance techniques that have been developed in the laboratories over the past three years. The advances in this area speak for themselves as most of the published work from this laboratory in the past three years has been directly associated with the development of this project. I should note that all results in articles 2, 4, 5 and 6 in this report represent unpublished results. In all instances, the results are new and of immediate concern in fundamental research in areas important to the ERDA mission.

2. THE SPECTROSCOPY OF MOLECULES ABSORBED ON METAL SURFACES

a. Spectroscopic Ellipsometry of Surface Adlayers in the Visible: Theory*

C. B. Harris, A. R. Gallo and D. A. Zwemer

When electromagnetic radiation impinges normal to an isotropic absorbed layer on a metal, to first order, the incident and reflected beams destructively interfere to give a node in the electric field at the surface. It would thus seem that an absorbed molecule would go undetected by optical spectroscopic methods. When one considers the full boundary problem at non-normal incidence angles, however, one finds appreciable fields at the surface.

We define the problem in detail as shown in Fig. 1. We use isotropic and smooth media with sharp boundaries for simplicity. The E's are composite amplitudes of mathematical sums of all the waves which travel in a given direction in each medium. Thus, we include the effects of multiple reflections within the absorbed layer in our calculations. From Maxwell's equations, and the boundary conditions that the tangential

Fig. 1. A schematic metal-surface-organic layer with incident radiation at an angle ϕ . (XBL 761-6323)

components of the $\vec{E}$ and $\vec{H}$ fields are equal at the interfaces, we arrive at a set of four-complex coupled equations in the field amplitudes. These equations can be solved by computer iteration procedures for a given set of optical parameters.

A more useful quantity than the field amplitudes for spectroscopic considerations is the absorption factor A , which is a measure of the depth of an absorption band in a spectrum. This quantity is defined in Fig. 2, where

$$R^0 = |\text{Re } E_x^-|^2 / |\text{Re } E_x^+|^2$$

Fig. 2. The absorption vs. wavelength. (XBL 773-7974)

is the reflectivity of the system when the adlayer is not absorbing (i.e., $k_2 = 0$). Experimentally, we obtain the reflection spectrum for the system by a transformation of the complex dielectric function.

Typical plots of the absorption factor vs. angle of incidence are shown in Figs. 3 and 4. The optical parameters chosen were for a polycrystalline Ni bulk substrate and an organic adlayer with a strong IR transition (Fig. 4) and a moderately weak electronic transition (Fig. 3).

We note the importance of the calculations in defining the optimum experimental angle of incidence. In Fig. 5 we note also the importance of the state of polarization of the incident light beam, the preferred polarization being the electric field parallel to the plane of incidence.

From the calculations, we have also obtained the phase shifts of the incident field upon reflection ψ (Fig. 6). Again we see a large dependence on the magnitude of the phase shift as a function of the angle of incidence. To

Fig. 3. The absorption coefficient vs. the angle of incidence for transitions in the visible. (XBL 761-6325)

Fig. 4. The absorption coefficient vs. the angle of incidence for transitions in the infrared. (XBL 761-6324)

Fig. 5. The relative absorption vs. the angle of incidence for parallel and perpendicular polarization. (XBL 762-6507)

Fig. 7. Phase shift vs. extinction coefficient for monolayer coverage. (XBL 7612-7955)

Fig. 6. Phase shift of the incident field upon reflection for parallel and perpendicular polarizations. (XBL 762-6503)

better appreciate the importance of this shift, in Fig. 7 we plot the phase shift for an absorption band minus the phase shift of the system when it is not absorbing, $\Delta\psi = \psi(k_2) - \psi(k_2 = 0)$, that is, away from an absorption band. For most electronic transitions, having molar extinctions coefficients in the order of 10^4 to 10^5 , we expect $\Delta\psi$'s around 0.4° . Experimentally, using a rotating analyzer ellipsometer we can measure $\Delta\psi$'s of around 0.002° . Thus this serves as a very powerful and sensitive technique to detect the absorption spectrum of the absorbed molecule.

b. UHV Instrumentation for Reflectance, Ellipsometry and Emission Spectroscopy at Low Temperatures*

C. B. Harris, A. R. Gallo and D. A. Zwemer

In the past year, an experimental system integrating ultrahigh vacuum, cryogenic and high precision optical technology has been developed for potentially powerful new techniques in the study of molecules adsorbed on surfaces. We have completed the first phase of the project, the construction of an UHV chamber (see Fig. 8)

Fig. 8. The ultra high vacuum surface spectrometer. (XBL 763-623)

with full capabilities for the cleaning and characterization of single crystal oriented metal or semiconductor surfaces using LEED, AES and quadrupole mass spectrometry. Base pressures below the design specification of 10^{-11} Torr and sample temperatures as low as 12 K have been achieved.

In the second phase of the project, we have constructed a rotating analyser photometric ellipsometer system coordinate to the chamber (see Fig. 9) which uses the shift in the

Fig. 9. Schematic of the surface spectrometer
utilizing spectroscopic ellipsometry.
(XBL 7612-7951)

polarization state of light in the UV to IR range upon surface reflection to determine (1) the absorption coefficients of substrate and adsorbed species, which identifies the adsorbate and the orbitals involved in surface bonding, (2) the surface index of refraction, which contains important information about charge carrier mobility and concentration at the surface, and (3) the adsorbate film thickness. The input leg of the ellipsometer includes light source, monochromator, and polarizer to establish the frequency and polarization state of the incident beam. After reflection from the sample surface, the light enters a rapidly rotating Glan-Taylor prism axially mounted in a frequency-stabilized synchronous motor with optically encoded reference, and a cooled phototube. An LSI-11 mini-computer, to be interfaced for both data acquisition and reduction, obtains complex reflectance data from Fourier transform digital analysis of the time dependence of the transmitted light intensity. The high speed, efficiency, and wavelength independence of the rotating analyser system allows wide spectral scans with final precision greater than 1 part in 10^4 .

Versatility has been an important criterion in the experimental design. In addition to ellipsometric and reflectance spectroscopy, the system may be easily adapted for laser- and electron beam-excited fluorescence and

phosphorescence of surfaces, including time-resolved measurements. Finally epitaxially-grown thick films as well as monolayer and submonolayer assemblies are available at the low sample temperatures.

* Partially supported by NSF.

3. ENERGY TRANSFER PROCESSES IN MOLECULAR SOLIDS

a. Energy Transfer Processes in Substitutionally Disordered One-Dimensional Solids: The Effects of Coherent and Incoherent Motion*

C. B. Harris and D. A. Zwemer

Energy transfer processes in all real systems, which range from photosynthesis to electrical conduction in semiconductors, must take account of chemical impurities, defects, and boundary effects which "disorder" the potential energy surface of the system. Previous work in this research group has shown that one type of energy transfer, the migration of triplet Frenkel excitons in molecular solids, is critically dependent on the modes of exciton propagation in a perfect crystal lattice. Our present study is a theoretical investigation of long-range migration in a more realistic model system containing two-component substitutional disorder (see Fig. 1). We have shown that the difference

Fig. 1. Schematic of a perturbed periodic potential for one-dimensional tunneling.

between the limiting mechanisms of (i) coherent propagation of an exciton wavepacket over many lattice sites and (ii) random walk exciton diffusion between adjacent lattice sites, retains reduced but still appreciable significance in the disordered crystal as compared to the perfect crystal.

The model system of Fig. 1 contains "barriers", representing chemical or isotopic impurities or crystal defects, which are identical (characterized by a constant transmission coefficient T) and periodic. To first order, long-range exciton migration may be treated as a Bernoulli random walk among intervals between barriers. Given our derivation of the exciton lifetime within an interval, exciton dynamics of this system are summarized by the diffusion coefficient

$$D \approx \frac{1}{2} S_1 a^2 \text{ Tv} \quad (1)$$

where ν is the intermolecular transfer frequency. Equation (1) is strictly valid only for a completely stochastic process, which requires that the exciton lifetime within an interval is sufficient to establish a uniform population density. In the regime $T \sim 1$, where this condition does not hold, the mode of exciton propagation, coherent or random walk, introduces additional correlation into exciton migration between intervals. The coherently-propagating exciton has a greater effective coherence length in its transfer between intervals. In contrast, random walk exciton diffusion on the intermolecular level increases the effective exciton lifetime in the interval. Exciton dynamics may again be characterized by the diffusion coefficients

$$D_c \equiv \frac{1}{2} \left(\frac{1-T}{1-T^2} \right)^2 T S_1 a^2 \nu \quad (2)$$

$$D_r \equiv \frac{1}{2} \left(1 - \frac{3}{2} S_1 T \right) S_1 T a^2 \nu \quad (3)$$

for coherent and random walk limits respectively. This is shown in Fig. 2. The coherent exciton

Fig. 2. Diffusion coefficient vs. transmission coefficient for tunneling. (XBL 768-7372)

shows more rapid long-range exciton migration than the random-walk exciton in the $T \sim 1$ regime, but also remains closer to the uncorrelated model because of the greater speed with which a uniform population density in the interval is achieved. The results obtained can be extended to a statistical distribution of barrier spacings and provide a basis for treating a heavily disordered lattice, as discussed in the following article No. 3b.

b. Experimental Studies in One-Dimensional Systems

C. B. Harris and D. A. Zwemer

We have investigated Frenkel exciton migration in the singlet and triplet bands in an isotopically mixed molecular crystal as a model for energy transfer in disordered systems. The experimental sample is shown schematically in Fig. 3. Our

Fig. 3. Schematic of tetrachlorobenzene mixed crystal system. (XBL 766-7105)

probe of the exciton dynamics in the pseudo-one-dimensional exciton conductor 1,2,4,5-tetrachlorobenzene (TCB) is the energy partitioning as shown by relative phosphorescence intensities between a low-concentration impurity, pyrazine, and the h_2 -TCB host. Excitation into the singlet band is accomplished with a conventional broadband source, while the forbidden transition directly into the triplet requires a high intensity pulsed dye laser.

For triplet excitation, the percentage of phosphorescence from the dilute impurity increases with increasing h_2 -TCB concentration (Fig. 4), demonstrating greater exciton mobility and communication between h_2 -TCB localized states. We have extended the theoretical results presented in the preceding article no. 3a to treat the case of heavily mixed crystals with a random distribution of the three components. A quantum tunneling model which includes resonant transfer across a statistical distribution of d_2 -TCB barriers can not accurately represent the experimental behavior in Fig. 4 within the temperature range examined. Such a model predicts a much sharper transition in impurity phosphorescence (Fig. 5). The alternative mechanism for long-range exciton migration involves thermal promotion and transfer through host barrier states. We are engaged in formulating a theoretical model for this mechanism which includes trap recurrence without transmission

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Fig. 4. Normalized intensity vs. composition.
(XBL 766-7110)

Fig. 5. Normalized intensity vs. composition for the tunneling model.
(XBL 766-7106)

and the concentration-dependent activation energy observed (Fig. 6) which we believe to be a previously unobserved effect.

Where competition between singlet and triplet manifolds for exciton migration occurs, the singlet may be much less efficient in the perfect crystal because of its short lifetime. In a substitutionally disordered crystal, the much greater bandwidth of the singlet may hide the perturbation of the potential surface and allow more efficient exciton transfer than the triplet.

Fig. 6. Normalized intensity vs. $1/T$ for crystals of different composition.
(XBL 766-7111)

Our experimental data for singlet excitation (Fig. 7) shows that $\sim 80\%$ of the excitons reach an impurity trap in the singlet state before intersystem crossing and that this percentage is independent of band composition over a wide concentration range. This is a novel demonstration of the "amalgamated band" limit which had been predicted theoretically.

Fig. 7. Normalized intensity vs. composition for singlet exciton motion.
(XBL 766-7108)

c. The Use of Thermal Modulation Spectroscopy in the Study of Triplet Energy Transfer Processes in Solids

A. R. Burns and C. B. Harris

In Fig. 8 is shown the temperature dependence of the phosphorescence emitted from the excited X-trap in 1,2,4,5-tetrachlorobenzene (TCB). The

Fig. 8. Normalized phosphorescence intensity emission from X-trap in H₂-TCB versus temperature. The curve represents a fit to the data using the parameters of the trap-exciton partition function. At temperatures above the lambda-point of 1+q. H_e, the phosphorescence intensity is too small to measure accurately. (XBL 7612-7966)

current model which accounts for this phenomenon of increasing delocalization with temperature involves the details of phonon-assisted trap-to-band promotion of the excitation energy. This model is depicted in Fig. 9. If a heat pulse is

Fig. 9. Kinetic model of phonon-assisted promotion of triplet excitation energy, localized in the X-trap of H₂-TCB, to the exciton band. (XBL 7612-7962)

generated at one end of the crystal, it will propagate through the crystal as a pulse of high-frequency phonons which will be absorbed by the trap molecules. Since the rate of localized energy promotion is increased by this higher density of phonons in resonance with the trap depth ($\Delta = 15 \text{ cm}^{-1} - 17 \text{ cm}^{-1}$), the intensity of the phosphorescence emission will decrease. It is thus possible to study the nature of the phonon-assisted transfer of excited triplet state energy by measuring the change in trap population resulting from the propagation of a well-characterized heat pulse.

The heat source in these experiments is a thin nichrome film deposited on a quartz substrate. One face of a flat (6 mm² square, 0.02 to 0.10 cm thick) slab of TCB is bonded to the heater film with Dow Silicone grease. The heater film can be

considered as a black body-type source of phonon radiation, the nature of which is completely analogous to the thermal radiation of photons. In the electromagnetic case, there is generally very little damping or scattering of photons in the usual transmission medium (air, vacuum). However, the transmission medium for phonons presents ample problems which will be discussed in another section. The important point to make here is that if the packet of phonons propagates ballistically (without phonon-phonon scattering) through the crystal, the frequency distribution of the phonons arriving at the opposite surface still corresponds to the temperature of the heater surface, even though the energy density of the pulse may be diminished by several orders of magnitude.

The phonon emission power per unit area of the heater surface is given by

$$\frac{P}{A} = \frac{\pi^5 k^4}{15 h^3} \left(\frac{e_L}{c_L} + \frac{2e_t}{c_t} \right) (T_H^4 - T_O^4) \quad (1)$$

T_H = heater temperature,

T_O = ambient bath temperature,

c_L, c_t = longitudinal, transverse phonon velocities,

e_L, e_t = phonon transmission coefficients of surrounding medium.

Ideally, one would like to directly measure the radiating temperature of the heater surface to see if the power of the heat pulse varies as T_H^4 . Since this is not possible with nichrome films, one is forced to measure the maximum temperature change experienced by a sensitive bolometer located in the vicinity of the heater film during a heat pulse. Thus, a calibrated (resistance vs. T) germanium film bolometer was bonded to the heater film surface with Dow Silicone grease and later bonded to the opposite face of flat TCB crystal sandwiched in between (see Fig. 10(a)). The maximum temperature change caused by a given heat pulse was measured from signals such as that shown in Fig. 11(a). Another method used to indirectly measure the change in heater temperature with input power was to measure the percent change in phosphorescence intensity ($\Delta I/I_{SS}$) as shown in Figs. 10(b) and 11(b). The quantity $\Delta I/I_{SS}$, when related to the I_{SS} vs. T curve in Fig. 8, gives a rough measure of the lattice temperature change.

One can see from the results shown in Table 1, that the detected temperature change of both the bolometer and the phosphorescence intensity varies as the one-quarter power of the heat pulse power. The decreasing value of B with increasing distance from the heater film is a result of large energy losses. It is clear from these results, that a more exact curve fit for the I_{SS} vs. T is needed in order to determine a reliable temperature change from the percent phosphorescence change. It is also possible,

THIN FILM GEOMETRY

Fig. 10. (a) A thin slab of single crystal TCB sandwiched between the heater and detector thin films. The films are vacuum evaporated onto glass substrates. The electrical connections to the heater film are made by evaporated gold films running down the side of the glass rod. The germanium film is connected to a constant current supply by way of solder connections to a second metal film in contact with the central germanium film. (b) Phosphorescence emitted by the crystal is monitored at right angles to the exciting light. (XBL 7612-7961)

Fig. 11. (a) Electrical response to temperature change experienced by the germanium bolometer film. The sharp peaks are pickup from the leading and trailing edges of the electrical pulse used to generate the heat pulse. (b) Decrease in phosphorescence intensity due to depletion of the x-trap population in H_2 -TCB. The long relaxation back to the steady state intensity is due to the combined slow rates of retrapping and singlet-to-triplet energy conversion ("feeding"). (XBL 7612-7960)

Table 1. Variation of observed $\Delta T_{max} = (T_1 - T_0)$ vs. input power.

Experiment	Power Range (W)	Actual Bath Temp (T_0)	$P = B (T_1^4 - T_0^4)$
Bolo/Heater (width = 0.4 msec)	0.005 - 0.53	2.0 K	$0.00169(T_1^4 - 1.95^4)$
Bolo/x-tal/Heater (width = 1.0 msec)	0.046 - 0.643	2.0 K	$0.0943 (T_1^4 - 1.98^4)$
(width = 0.10 msec) 0.025 cm thick	0.286 - 2.571	2.0 K	$0.917 (T_1^4 - 2.00^4)$
x-tal phos $\Delta I/I_{ss}$ (width = 1.0 msec)			
0.08 cm thick	0.11 - 2.73	2.0 K	$0.140 (T_1^4 - 2.03^4)$
0.05 cm thick	0.27 - 1.08	2.0 K	$0.235 (T_1^4 - 2.01^4)$
0.05 cm thick	0.27 - 1.08	1.75 K	$0.203 (T_1^4 - 1.78^4)$
0.05 cm thick	0.27 - 1.08	1.48 K	$0.192 (T_1^4 - 1.66^4)$

however, that the maximum phosphorescence change does not really correspond to a new steady state value, and that the use of the I_{ss} vs. T is not really valid. This remains to be determined.

The spectral frequency distribution of the net flux of phonons into an ideal transmission medium is shown in Fig. 12 for various heater temperatures T_H above the ambient bath temperature of 2 K.

Fig. 12. Calculated phonon flux emitted by an ideal blackbody radiation as a function of frequency. The metal film is assumed to be at a constant temperature which is ΔT above that of surroundings. The phonon velocities used here are those for nickel. (XBL 7612-7963)

The flux of phonons of frequency ν is given by the expression:

$$\frac{N(\nu)}{A} = 2\pi\nu^2 \left[\frac{1}{c_L^2} + \frac{2}{c_t^2} \right] \left[\frac{1}{\exp(h\nu/kT_H) - 1} - \frac{1}{\exp(h\nu/kT_0) - 1} \right] \quad (2)$$

If, for simplicity, one sets the bath temperature T_0 equal to zero, the spectral radiation power is given by

$$P(\nu) = h\nu N(\nu) = \frac{2\pi h \nu^3}{\exp(h\nu/kT) - 1} \left[\frac{1}{c_L^2} + \frac{2}{c_t^2} \right] \quad (3)$$

Since the frequency maximum of the radiation increases linearly with the heater temperature according to Wien's displacement law

$$\nu_{\max} = \frac{2.82 kT_H}{h}$$

the radiant power at the frequency maximum will be

$$P(\nu_{\max}) = \frac{2\pi\nu_{\max}^2}{e^{2.82} - 1} \left[\frac{1}{c_L^2} + \frac{2}{c_t^2} \right] \quad (4)$$

By substituting Eq. (4) and Eq. (1) into Eq. (5) one is able to solve for the total power dependence of the maximal spectral power:

$$P(\nu_{\max}) = (2.67 \times 10^{-11}) p^{0.75} \quad (5)$$

Now the half-width of the maximal spectral power is on the order of $\nu_{\max}$, which for a heater temperature of 5 K is about $3 \times 10^{11} \text{ sec}^{-1}$. Thus one can see that a large part of the total power dissipated in the heater film is in a fairly sharp region centered around kT_H/h .

The power dependence of the signal detected by the X-trap phosphorescence change is shown in Fig. 13, along with the power dependence of the

Fig. 13. Power dependence of the maximum of the germanium detector response when the detector film is bonded to the crystal surface as in Fig. 10(a). Also shown is the power dependence of the maximum decrease in X-trap phosphorescence. In both experiments, the heat pulse width was 1.0 msec. (XBL 7612-7964)

bolometer signal. One can see that the almost linear power fits for each set of data are slightly different. This difference is most likely due to the nature of the phonons absorbed by the different detectors. The bolometer will absorb phonons of all frequencies since the phonon-electron interaction giving rise to the change in resistance is not expected to have a frequency dependence. However, if the promotion of trapped triplet energy is essentially a one-phonon process, then only phonons resonant with the trap depth ($\Delta = 15-17 \text{ cm}^{-1}$) will be detected and also the signal observed should almost be linearly dependent on the total power.

d. Direct and Indirect Energy Transfer Processes in One-Dimensional Solids

C. B. Harris and M. T. Lewellyn

Recent studies have focused on the investigation of processes involved when an excitation in

a localized state is promoted to the exciton band and becomes mobile. This promotion is known to be an important mechanism for energy transfer in solids and is intimately related to the question of whether or not statistical models can be used to describe the relative populations of various energy states in solids.

Past studies on 1,2,4,5-tetrachlorobenzene mixed crystal systems (see Fig. 14) using the

Fig. 14. Phonon-assisted tunneling between localized states. (XBL 7611-7788)

coherent spectroscopic techniques, have been concerned with promotion processes from the deep (h_2) localized state to either the shallow (h_d) states or the delocalized band (d_2) states. We have shown that this promotion is influenced by both temperature and isotopic concentration. The temperature dependence derives from the nature of the promotion process which involves the interaction of lattice phonons with the trap population.

Our attempts to conduct similar studies on the "shallow" state have been frustrated by an inability to coherently drive the spin polarization between two of the shallow state's zero-field spin sublevels. By utilizing both steady state luminescence measurements and continuous wave optically-detected magnetic resonance techniques however, we have established that promotion processes out of the shallow state occur almost exclusively to the band states. The rate of promotion at a given temperature is much faster than that for the deep state. This rate increase is due, in part, to the reduced activation energy required for promotion to the band states from the shallow trap; however, there are also indications that the temperature-independent matrix elements associated with phonon interactions differ for the two trap species.

4. COHERENT SPECTROSCOPY IN EXCITED TRIPLET STATES

a. Applications to Energy Transfer Processes

C. B. Harris

The information one can obtain from conventional molecular spectroscopy is generally limited in at least one important way. Observations are usually made on an inhomogeneous line; hence, the time dependent correlation function

describing physical phenomena that are responsible for energy fluctuations of states cannot be obtained directly from the line shape or line width. The net result is that the important interrelationships between the time dependent molecular Hamiltonian and line shape transform theories cannot be exploited. The power of coherence techniques lies in their ability to remove certain unwanted interactions from consideration, such as the inhomogeneous contributions to the linewidth or in the case of excited triplet states, effects from nuclear spin diffusion, laying bare the effective linewidth that results from the relaxation time of phenomena of more immediate interest. For example, if a kinetic process such as energy transfer or vibrational relaxation affects the electron spin coherence in a time fast compared to other dephasing phenomena in a particular coherence experiment, then the Fourier transform of the relaxation spectrum yields a homogeneously narrowed line that is centered at the zero field transition frequency and that has a width that is related to rate parameters for energy transfer. In this sense the time dependent field the spins are subjected to remove unwanted contributions to the line width and narrows the EPR transition to a point where its residual width is due only to the kinetic process itself.

A prerequisite however for studying kinetic phenomena with coherent spectroscopy is that the effective Hamiltonian responsible for the decay of the electron spin coherence be also responsible for the phenomena one is interested in investigating. Since hyperfine interactions and nuclear spin diffusion dephase the triplet spins on a time scale of about 10 microseconds, either the relaxation time of the kinetic events must be shorter than this, or one must use one of the methods we have described for removing the nuclear interactions.

The coherence method one chooses to use depends somewhat on the range of relaxation times one expects from the kinetic phenomena. In principle, optically detected spin-locking and optically detected adiabatic demagnetization in the rotating frame (ADRF) would suffice for most problems. Spin locking is not restricted to short times and can be performed down to several hundred nanoseconds. ADRF is practically limited, however, from experimental considerations to ~ 200 microseconds to 1 second. In all methods the correlation time of the technique can be controlled by the cycle time which in turn is controlled by the strength of the applied field γH_1 . Since nuclear spin diffusion affects the electron spin coherence in a characteristic time of 10 microseconds, one needs an γH_1 field of about 0.5 MHz to remove fluctuating hyperfine fields from consideration. Under these circumstances kinetic phenomena that dephase the spins in the range 100 nanoseconds to 500 microseconds can be investigated. Relaxation times longer than 500 microseconds can be measured if γH_1 is increased to about 5 MHz to insure a complete removal of nuclear spin effects.

It is not our purpose in this report to go into great detail on the myriad of interesting

questions that arise in the area of energy transfer dynamics in solids but rather to illustrate how coherent spectroscopy can provide qualitative insight and quantitative information on the routes and mechanisms for the processes. The most effective use of coherence techniques is in combination with each other and with conventional methods. Coherence techniques are like the surgeons' tools. Each has an advantage in a particular circumstance, but the dissection of a problem requires the careful interplay of the techniques at the hands of a skilled experimentalist. A few of these areas have been outlined below. Although the experimental systems are different, the principles of the methods are the same and thus they form a powerful approach to solving many varied problems in chemical dynamics in both ground and excited states.

b. Phonon Promotion Processes*

H. C. Brenner, C. B. Harris and D. A. Zwemer

A good understanding of triplet exciton migration in a particular system requires knowledge of the structure and energy of imperfections in the crystal lattice. When an imperfection is sufficiently complex, its structure may not be accessible from simple optical spectroscopy and more sophisticated probes of its structure and excited state geometry are necessary. We have characterized several chemical impurity-induced "Y traps" in 1,2,4,5-tetrachlorobenzene (TCB) using a variety of new techniques. The impurities used to induce the Y trap are 1,4-dichlorobenzene (DCB), 1,4-bromochlorobenzene (BCB), and 1,2,4,5-tetrabromobenzene (TBB). The Y trap itself shows full TCB vibrational structure, but its phosphorescent intensity is proportional to the concentration of the added impurity. The Y trap is therefore a TCB molecule perturbed by a nearby impurity which is not seen in the phosphorescent emission.

Many of the techniques used have been pioneered in these laboratories: optically-detected electron spin resonance, phosphorescence-microwave double resonance (PMDR), microwave-induced delayed phosphorescence (MIDP), optically-detected spin locking, and adiabatic demagnetization in the rotating frame. From the PMDR and MIDP results, we can predict the lowered symmetry of the excited Y trap as compared to an isolated TCB molecule. The ESR spectra show population transfer between Y trap and impurity which defines their spatial relationship. Spin-locking distinguishes the limits where the chemical impurity has an energy comparable to that of the Y trap (4 cm^{-1} higher in the case of TBB/TCB Y trap) and where the impurity energy is much greater (see Fig. 1).

The Y trap structures as revealed by these experiments are obviously of critical importance to exciton dynamics in these systems. The presence of high energy barriers such as appear in BCB/ and DCB/TCB Y traps is particularly important in one-dimensional systems, because they divide the host band into isolated states

Fig. 1. Schematic of the host and impurity band distribution in the Y-trap of 1,2,4,5-tetrachlorobenzene. (XBL 768-7479)

in which a triplet exciton is effectively trapped over the excited state lifetime. In such cases the possibility of macroscopic exciton diffusion is eliminated. The structure of a TBB/TCB Y trap, while spectroscopically similar, is such that excitons may cross between localized host band states in long-range exciton diffusion. Optically detected magnetic resonance spectroscopy is shown to be an extremely useful tool in characterizing the energy transfer properties of molecular solids.

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c. Tunneling Studies

C. B. Harris and M. E. Tarrasch

Exchange processes in spin systems which occur on a timescale slower than 10^7 sec^{-1} are usually masked by the EPR line widths and preclude a line shape analysis. Optically detected spin coherence techniques developed in these laboratories are capable of extracting the exchange rate directly from a time resolved experiment, and have been applied to configurational tunneling in cyclopentanone.

It has been claimed (Shain and Sharnoff, 1973) that quantum mechanical tunneling between different conformations in cyclopentanone occurs between $5 \times 10^2\text{ sec}^{-1}$ and $5 \times 10^7\text{ sec}^{-1}$. In an attempt to get a quantitative value for the exchange rate, the D-|E| transition at 3394.4 MHz was spin locked at different temperatures. Figure 2 illustrates the temperature dependence of the spin locked ensemble lifetime T_{10} . Within experimental error, T_{10} is temperature independent and decays with a lifetime of $\sim 3\text{ msec}$. The decay and the corresponding Fourier transform illustrated in Fig. 3 demonstrate that the line width has been reduced by four orders of magnitude. If tunneling occurs on the time scale proposed by Sharnoff, it should be observable; however T_{10} values between 1.4 K and 4.2 K were lifetime limited, indicating that either extremely rapid or slow exchange is occurring.

It has been shown that the observed decay rate is governed by $k_{\text{eff}} = k_{\text{ave}} + W_+$ for slow exchange and $k_{\text{eff}} = k_{\text{ave}} + W_+(\delta\omega\tau)^2$ for fast exchange. k_{ave} is the lifetime limit for the triplet state,

Fig. 2. Temperature dependence of $T_{1\rho}$ $n\pi^*$ state of cyclopentanone.
(XBL 768-7296)

Fig. 4. EPR transition frequency vs. temperature.
(XBL 768-7958)

Fig. 3. (A) Coherent component of the spin locked state of cyclopentanone vs. time.
(B) Fourier transform of the decay time.
(XBL 768-7295)

W_+ is the rate of exchange, τ is the time the spin is in a different environment, and $\delta\omega$ is the difference in Larmor frequencies for the two configurations. Using values of 205 MHz for $\delta\omega$ and 402 sec^{-1} for k_{ave} , τ would have to be 10^{-15} sec in order to be in the fast exchange limit. This is clearly impossible since one can resolve EPR lines 205 MHz apart. Indeed, if τ were shorter than 10^{-9} sec , a frequency shift in the EPR absorption would be observable. Figure 4 shows the frequency of the D-|E| transition vs. temperature, once again indicating neither a shift nor a temperature dependence. A value of 10^{-15} sec for τ would cause the EPR lines belonging to the different configurations to merge, which is not observed.

In the limit for slow exchange, τ would have to be $\sim 25 \text{ msec}$ to account for the value obtained for k_{eff} ; this is ten times longer than k_{ave} , the lifetime for decay to the singlet ground state. Thus, an excited cyclopentanone molecule will, on the average, decay via phosphorescence or some non-radiative process before tunneling to an isoenergetic configuration.

We have demonstrated that optically detected spin coherence is a powerful technique for investigating energy exchange problems and shown that configurational tunneling in cyclopentanone does not occur on a time scale comparable to the triplet lifetime.

5. THERMAL MODULATION SPECTROSCOPY

a. Coherent Heat Transport in Solids at Low Temperature

A. R. Burns and C. B. Harris

In a previous article No. 3(c) it was noted that if the propagation of phonons was essentially unobstructed in a molecular crystal, then the frequency spectrum of the phonon radiation emitted by a heat source at one face of the crystal will be observed at the opposite face. This limit of unobstructed phonon propagation is usually referred to as ballistic thermal transport (Coherent Flow). The other limit of thermal transport is classical heat diffusion. In the framework of these two limits, one may assign a mean free path, ℓ , in a crystal for phonons traveling with a mean velocity $\bar{V}$ according to the expression:

$$K = 1/2 S \rho \bar{V} \ell \quad (1)$$

In order to determine the mean free path of the phonons at a particular temperature of the

lattice, the thermal conductivity K and the specific heat S of the transmission medium must be known. Since the mean free path ℓ can be expressed in terms of a time $\tau = (\ell/\bar{V})$, research has concentrated in the study of phonon interactions which limit the time τ between scattering events, and thus limit the bulk thermal conductivity of the crystal. The phonon scattering rate τ^{-1} is actually a sum of all the rates due to the various scattering processes, some of which are in the equation below:

$$\tau^{-1} = AW^4 + B_1W^4T^3e^{-\theta/aT} + \bar{V}/L. \quad (2)$$

The first two-frequency dependent terms respectively represent the rate of phonon scattering at crystal defects, which include isotopic impurities, and the rate of phonon-phonon scattering. Phonon-phonon scattering is highly temperature dependent, since the number of phonons available increases with temperature. The third term represents boundary scattering, which occurs at a rate governed by the mean velocity and the bulk crystal dimension L . Ballistic or coherent thermal transport occurs when τ^{-1} is governed by $\bar{V}/L$; whereas diffusive thermal transport is the result when τ^{-1} is dominated by phonon-defect and/or phonon-phonon scattering.

Countless measurements have been made of the phonon mean free path in high purity crystals at low temperatures using the techniques of steady-state thermal conductivity measurements. In the last ten years, however, the technique of time resolved heat pulses has been used to directly measure the transit time of the thermal carriers. At very low temperatures (< 10 K) two sharp pulses can often be resolved if the heat pulses are less than 0.1 μsec long. The two sharp pulses refer to the longitudinal and transverse phonon modes traveling at their respective velocities V_ℓ and V_t . These observations are possible only when the coupling between the heater and the crystal, as well as the coupling between the bolometer and the crystal, is strong enough such that the response times are shorter than the phonon transit times ($\sim 1 \mu\text{sec}$). The strong coupling is made possible by the direct evaporation of the metal films on the crystal faces, which results in interface conductivities on the order of $0.40 \text{ T}^3 \text{ W/K}^0\text{-cm}^2$.

In order to determine the thermal conductivity of an aromatic hydrocarbon crystal by the heat pulse method, the heater and detector films must be evaporated on to separate quartz substrates and then bonded to the faces of the crystal as shown in Fig. 10 of preceding article No. 3c. The thermal coupling of the metal films to the crystal faces is accomplished by a thin layer of Dow Silicone grease. The thermal conductivity of a Dow Silicone grease mediated thermal contact has been reported to be $0.0037 \text{ T}^3 \text{ W/cm}^2\text{K}$ in conventional steady-state measurements, which is two orders of magnitude lower than that mentioned above. Thus instead of measuring the actual transit time of a short phonon pulse, one must instead measure the risetime of the crystal lattice temperature. The response time of the

crystal lattice to a μsec heat pulse will thus be equal to the ratio of the TCB heat capacity to the total conductance between the heater and the detector, K_{tot} , given by

$$\frac{1}{K_{\text{tot}}} = \frac{1}{K_{\text{TCB}}} + \frac{2}{K_{\text{interface}}} \quad (3)$$

$$\tau_R = \frac{C}{K_{\text{tot}}}$$

The factor of 1/2 for the interface conductivity is due to the fact that one must take account of both the heater/crystal interface and the crystal/bolometer interface. The risetime of the thermal response of the lattice, such as that shown in Fig. 11(a) preceding article No. 3(c) is found by obtaining the best fit to the exponential $\Delta T_{\text{max}}(1 - e^{-t/\tau})$. The bath temperature dependence of this risetime can be used to determine the temperature dependence of the lattice and boundary conductivities provided the lattice heat capacity is known. The lattice heat capacity of TCB in the temperature range 0.5 to 7.0 K, was recently determined in collaboration with Professor Phillips's group. The thermal conductivities for a 0.025 cm thick and 0.06 cm^2 in cross-sectional area TCB crystal are shown in Fig. 1.

Fig. 1. Thermal conductivity and boundary interference conductivity in tetrachlorobenzene.

(XBL 7612-7959)

By using the known values of the TCB heat capacity, and its temperature dependence to extract a mean acoustic velocity $\bar{V}$, one can predict the lattice thermal conductivity if one also assumes that at these temperatures, the mean free path equals the crystal thickness of 0.025 cm. In this way the lower values of the interface conductivity are calculated from K_{tot}

and τ_R . The best fit of the temperature dependence of the interface conductivities is very close to the steady-state measurement of $0.0037 \text{ T}^3\text{W/cm}^2\text{K}$ cited earlier. Thus it appears that the assumption of a crystal thickness-limited mean free path in these TCB samples is justified.

The fact that the flow of heat through these samples appears to be ballistic is not surprising in view of the very high purity of the material. Only extensively zone refined material was used, and other experiments have shown that the crystal defect concentration along the linear chains of the lattice may be as low as one part per 100,000. Another reason explaining the high thermal conductivity is that the ambient bath temperature is low enough such that the phonon-phonon scattering rate is below that required to effect the conductivity.

b. The Determination of Heat Capacities Using Thermal Modulation Techniques

A. R. Burns and C. B. Harris

It was demonstrated in the preceding article No. 5a that the risetime of a thermal pulse in a crystal is a function of the lattice heat capacity and the total thermal conductivity of the crystal lattice and respective heater and bolometer interface conductances. The work presented there involved the use of a bolometer assumed to be in thermal contact with the crystal lattice. In this article, it will be demonstrated that thermophysical quantities such as the heat capacity can be found by analyzing the time resolved response of an intrinsic temperature sensor which manifests its response optically. This intrinsic detector is the well-documented excited triplet band-trap state system. The time-resolved phosphorescence response of this system is shown in Fig. 11(b) of preceding article No. 3c.

The "response" time of this system is governed by the kinetics of the process by which the localized excitation is promoted to the upper band states. However, since a heat pulse results

in a tremendous flux of phonons of relatively high energy with respect to the ambient bath temperature, the rate of thermal delocalization of excited triplet energy is so enhanced that it becomes limited by the lattice or bulk crystal thermal response time. Thus it becomes possible to actually measure the crystal lattice heat capacity by measuring the risetime of the phosphorescence change.

Since the thermal conductance of the crystal is essentially governed by its bulk dimensions, it is possible to increase the thickness of the crystal to the point where its thermal conductance is so much larger than the heater/crystal conductance, that it may be disregarded in the calculation of K_{tot} (see Eq. (3) in the preceding article No. 5a. When this is the case, the heat capacity of the molecular crystal can be calculated directly from the known interface conductance K_{bound} and the phosphorescence decay time τ_R .

The results of the best fit exponential phosphorescence decays of a series of crystal samples of varying thicknesses are shown in Table 1. The values of K_{boundary} were calculated from those obtained in the preceding article No. 5a ($K_{\text{bound}} = 3.4 \text{ T}^{3.2} \text{ mj/sec cm}^2\text{K}$). One can see that the risetime increases linearly with the sample thickness, as expected for $\tau_R = C/K_{\text{tot}}$. However, the values of the heat capacities obtained by this technique are one-half the actual values. The most reasonable suspects for this discrepancy are the boundary conductivities but in light of the agreement with the literature values, one cannot dismiss them. Another reason for the discrepancy may be due to a fundamental difference in the nature of the two detectors involved; i.e., the phosphorescence changes are the result of the absorption of relatively high energy phonons ($15\text{-}17 \text{ cm}^{-1}$), whereas the germanium bolometer "sees" all phonon frequencies. It has been observed in other laboratories, that the high frequency phonons have a higher transmission coefficient through boundaries than do the lower frequency modes. It is thus possible that the boundary conductivity measured here by the phosphorescence changes is only for high-frequency modes. The values listed in Table 1 can be compared to the results of a direct heat capacity measurement shown in Fig. 2.

Table 1. Heat capacities from optically detected thermal risetimes.

T	L	A	msec τ_R	$\mu\text{j/k}^\circ$ k_{bound}	$\mu\text{j/k}^\circ$ C_{obs}	$\mu\text{j/k}^\circ$ C_{ss} (Phillips)
2.0 K	0.03	0.06	0.147 ± 0.31	1.87	0.275	0.472
2.0 K	0.04	0.06	0.20 ± 0.04	1.87	0.374	0.630
2.0 K	0.05	0.06	0.260 ± 0.035	1.87	0.486	0.787
1.75	0.05	0.06	0.272 ± 0.055	1.22	0.332	0.535
1.48	0.05	0.06	0.211 ± 0.032	0.72	0.152	0.328
2.0 K	0.08	0.06	0.414 ± 0.052	1.87	0.774	1.259

Fig. 2. Heat capacity vs. temperature in tetrachlorobenzene. (XBL 7612-7965)

6. PICOSECOND SPECTROSCOPY

a. Studies of Coherence and Relaxation Processes in Condensed Phases

P. A. Cornelius, C. B. Harris and R. M. Shelby

An excited molecule in a condensed phase (solid or liquid) is in intimate contact with its neighbors and as such its excitation energy is strongly influenced by fluctuations in the intermolecular interactions. The time dependence of these interactions is responsible for an initial coherent state ultimately returning to thermal equilibrium following the excitation event.

For example, consider a molecule in a crystal with a single quantum of excitation in a particular intramolecular vibrational mode. Intermolecular interactions in the condensed phase allow resonant vibrational energy transfer to neighboring molecules, and a proper description must account for the delocalization of the excitation. This phenomenon can be understood in terms of exciton dynamics if one properly includes nonradiative decay into other intramolecular modes or into lattice vibrations with different energies. The degradation of the energy to lower-frequency modes is one mechanism for the loss of phase coherence of the excited molecules. In effect, the lattice periodicity is disrupted by the vibrations of the molecules. In the limit where this effect is dominant the behavior of a solid and a liquid are similar, and the exciton idea is less useful. We have been investigating the relative importance of these interactions and their relationship to energy transfer and vibrational relaxation.

As an initial step in attaining this objective, the techniques of picosecond laser spectroscopy have been utilized in a variety of condensed phase systems to directly measure the vibrational relaxation times associated with the loss of

population (T_1 processes) and the loss of phase coherence of the excited molecules (T_2 processes). These processes are shown schematically in Fig. 1 for the molecular crystal case. The

Fig. 1. (a) Some typical dispersion relations for intramolecular vibrations (vibrational excitons) and lattice modes (phonons) are shown schematically. (b) The state prepared by the stimulated Raman scattering excitation process is indicated. The double arrows indicate relaxation processes leading to loss of excited population (T_1 processes) and loss of phase coherence through scattering of the excitation to other k -states (T_2 processes). (XBL 7612-7940)

technique (von der Linde, Laubereau, and Kaiser, 1971) involves preparation of an ensemble of coherent vibrationally excited molecules via stimulated Raman scattering of a short (4×10^{-12} sec) laser pulse. The coherent nature of the excitation mechanism establishes a well-defined phase relationship among the excited molecules. The excitation process and the energy levels involved are shown schematically in Fig. 2. The time evolution of the ensemble of excited molecules is monitored through anti-stokes Raman scattering of a second suitably delayed laser pulse (see Fig. 2). If the anti-stokes waves due to scattering by different molecules are in phase, the anti-stokes signal is coherent, and the probing process monitors the dephasing of the ensemble thus providing a measurement of T_2 . The phase matching requirement can be satisfied by choosing the experimental geometry such that the wavevectors of the excitation, probe, stokes and anti-stokes beams add up vectorially as shown in Fig. 4. On the other hand, in a non- k -vector matched direction the anti-stokes emission is incoherent, the decay of the excited population is monitored, and T_1 is measured. A typical experimental set up for these measurements is shown in Figs. 3 and 4.

In order to carry out these experiments and properly interpret the results, the laser pulses must be well-characterized in terms of spatial and temporal coherence, pulse width and pulse shape. We have constructed a TEM₀₀ Mode mode-

(a) STIMULATED RAMAN SCATTERING; EXCITATION AND PROBING PROCESSES

(b) WAVE VECTOR MATCHING GEOMETRY FOR COHERENT ANTI-STOKES SCATTERING

Fig. 2. (a) Energy levels involved in Raman excitation and probing are the ground state ($V=0$) and a vibrationally excited state ($V=1$). Excitation involves scattering events in which a laser photons (frequency = ω_L) is absorbed and a Stokes photons (frequency = ω_S) emitted thus transferring population from $V=0$ to $V=1$. In the probing process photons are absorbed from the probe pulse and anti-Stokes photons are emitted (frequencies ω_p and ω_{AS} respectively). The vibrational excitation remaining in $V=1$ is measured in this way. (b) The wave vector geometry necessary to observe coherent anti-Stokes scattering is shown. k_{vib} is the wave vector of the vibrational excitation prepared by stimulated Raman scattering. (XBL 7612-7944)

MODE LOCKED Nd-GLASS LASER SYSTEM

Fig. 3. Diagram of the Nd-glass laser system. Laser components: M_1 = rear mirror, D = model-locking dye flow, A = aperture, L = Nd-glass laser rod, M_2 = partially transmitting front mirror. Pulse selection components: $\lambda/2$ = quartz half-wave plate, GP = Glan-Thompson polarizer, PC = Rockel's Cell, SG = Laser triggered spark gap, BS = beam splitter. Amplifiers and Second harmonic generation: A_1 & A_2 = Nd-glass amplifier rods, KDP = KH_2PO_4 frequency doubling crystal. (XBL 7612-7942)

MEASUREMENT OF VIBRATIONAL DEPHASING TIME (T_2) USING COHERENT ANTI-STOKES SCATTERING

Ref: von der Linde, Laubereau and Kaiser, Phys. Rev. Lett., 26, 954 (1971)

Fig. 4. Diagram of the set-up used for dephasing time measurement. BS = beam splitter, DL = optical delay line, T_1 & T_2 = Gallilean telescopes, F_1 , F_2 & F_3 = filters, $\lambda/2$ = quartz half-wave plate, PMT_1 , PMT_2 & PMT_3 = photomultiplier tubes which monitor the laser intensity, Stokes intensity and anti-Stokes intensity respectively, S = sample, SP = 3/4 meter spectrometer, A = aperture. (XBL 7612-7941)

locked neodymium glass laser with capability for single pulse selection and amplification and second harmonic generation. This laser provides single mode-locked pulses of duration 4×10^{-12} sec and total energy 20 mJ. Measurements on the second harmonic pulses have shown their frequency width to be determined by the uncertainty principle, i.e., their coherence is limited only by their pulse width and no sub-picosecond structure is present. To obtain information about the detailed shape of the laser pulses, it is useful to consider the nature of the stimulated Raman excitation process in the coherent anti-Stokes experiment described above. The theory of this process has been known for some time, and it has been shown (von der Linde and Laubereau, 1971) that when T_2 is much less than the laser pulse width, the experiment gives the pulse shape. Data obtained in these laboratories for the C-H stretching vibration of ethanol are shown in Fig. 5 along with a theoretical fit to the data. The laser pulse shape was varied for the best fit to the experimental data with T_2 held constant. This resulted in the pulse shape shown.

We have obtained preliminary data for the coherent scattering on some systems of interest including the methylated benzenes. The data is for the methyl C-H stretch of p-xylene (p-dimethylbenzene), a liquid at room temperature, and liquid and solid durene (1,2,4,5-tetramethylbenzene). The experimental data are fit using the pulse shape determined in the ethanol experiment (Fig. 5) and allowing the value of T_2 to vary. The best fits are illustrated in Figs. 6, 7 and 8 respectively. The solid durene and liquid durene curves can be fit for T_2 in the range 0.25 to 0.75 psec, while the p-xylene data indicates $T_2 \sim 2.0$ psec. It should also be noted that these values also place lower bounds on the

COHERENT ANTI-STOKES SCATTERING IN ETHANOL

Fig. 5. Coherent anti-stokes scattering data for the C-H stretching mode of ethanol. The normalized anti-stokes signal is plotted as a function of probe pulse delay time. The theoretical fit indicates that our laser pulse intensity can be represented as a Gaussian rise [$I_1 = I_0 \exp(-(t/6.34 \text{ psec})^2)$ for $t \leq 0$] and an exponentially falling tail ($I_1 = I_0 \text{sech}(t/3.94 \text{ psec})$ for $t \geq 0$). (XBL 7612-7950)

COHERENT ANTI-STOKES SCATTERING IN DURENE (LIQUID)

Fig. 7. Coherent anti-stokes data for liquid durene just above its melting point. The data can be fit using $T_2 = 0.25 \text{ psec}$. (XBL 7612-7947)

COHERENT ANTI-STOKES SCATTERING IN p-XYLENE

Fig. 6. Coherent anti-stokes data for methyl C-H stretch in p-xylene. Using the pulse shape previously determined (see Fig. 5) a value of T_2 is determined. This value and those for durene (Fig. 7 and 8) are probably accurate to within a factor of 2. (XBL 7612-7948)

COHERENT ANTI-STOKES SCATTERING IN DURENE (SOLID)

Fig. 8. Coherent anti-stokes data for methyl C-H stretch in crystalline durene at room temperature. The theoretical fit gives $T_2 = 0.75 \text{ psec}$. (XBL 7612-7949)

corresponding values of T_1 . Although dephasing times in this regime cannot be more accurately determined with our pulses, one notes no substantial difference between the T_2 values for liquid and solid durene. This is not surprising in this temperature regime, since similar behavior for the liquid and the solid might be expected on physical grounds.

The determination of the contribution of T_1 to the dephasing and the investigation of the importance of phonon scattering through low temperature studies are in progress as well as low temperature spontaneous Raman line width studies and isotopic substitution experiments. These are being developed to investigate the effect of isotopic impurities. With these data, we are beginning to put together an understanding of vibrational coherence in solids and the effects of intermolecular interactions in these systems.

b. Studies of Electron Hole Recombination Rates in Semiconductors

C. B. Harris and E. D. Liu

Conversion of light energy to chemical energy is an important practical problem of scientific interest. It has been reported that (Fujishima and Honda, Nature 238, 1972) ultraviolet irradiation on a n-type semiconductor TiO_2 electrode of an aqueous electrochemical cell can evolve O_2 at the TiO_2 electrode and H_2 at the Pt electrode. The TiO_2 electrode serves as a catalyst in the reaction of photo-decomposition of H_2O , or so called photo-electrolysis of H_2O . As shown in Fig. 9 the photo-generated hole-

Fig. 9. The energy levels for photoelectrolysis on semiconductor surfaces. (XBL 7612-7957)

electron pairs do not recombine but are separated by the energy band bending at the interface of the TiO_2 electrode with the electrolyte; the electrons move away from the surface into the bulk of the semiconductor and then through the external circuit to the Pt cathode, where H_2 is generated; while the holes remain at the surface of the semiconductor anode, where they can interact with the electrolyte to produce O_2 . We have set up a series of combined laser surface experiments to study (i) the role of band bending

present at different surfaces of TiO_2 single crystals to the photoelectrolysis process; (ii) the location of the active site for this process; and (iii) electron diffusion rates from the surface to the bulk as a function of the position of the pinned Fermi levels to quantitatively relate the photo yield of O_2 and H_2 to the Fermi level and the electron-hole recombination rates.

We have used ellipsometry combined with a picosecond mode locked ruby laser or a nanosecond dye laser pumped by a N_2 laser to measure the change of the refractive index of the sample surface with a probing pulse following the absorption of an intense excitation pulse in the band gap.

Figure 10 shows a sketch of the experiment. An ellipsometer consists of two Glan-Thomson

Fig. 10. Dye laser ellipsometric spectroscopy on titanium dioxide surfaces. (XBL 7612-7954)

polarizer prisms and a quartz quarter wave plate. A N_2 laser, operating at 10 Hz repetition rate with 10 nanosecond pulse duration, was used as the excitation pulse, while a dye laser (nile blue 8×10^{-4} M + Rodamin B 4×10^{-3} M), operating at 6943 Å, was used as probing pulse. The incident angle of the probing beam was kept between 65° and 70° , while the exciting beam was close to normal incidence. The intensities of both pulses were measured with photodiodes or photomultiplier tubes and averaged. The absolute power intensity of the exciting pulse was measured by a laser power meter with an iris placed at the position where the sample was. Samples with (100) or (001) surfaces, as determined by the x-ray diffraction techniques were cut from a TiO_2 single crystal obtained from National Lead Industries. All the surfaces were mechanically polished by using $0.5 \mu \text{Al}_2\text{O}_3$ powders and then

cleaned with 6 M H_2SO_4 . Samples were then baked at 650°C under vacuum (10^{-6} mm Hg) for three hours to be converted to n-type semiconductors. In the present experiments, samples are immersed in aqueous solutions in a glass cell. Initially the ellipsometer analyzer and polarizer prisms were adjusted for a very sharp extinction ratio (10^{-4}) with no excitation pulse. The absorption of the N_2 laser excitation pulses in the crystal produced an increase in the probe beam transmission since the creation of charge carriers at the semiconductor surface changes the polarization of the reflected probe beam. From the magnitude of the change of the angle readings of polarizer and analyzer prisms of the ellipsometer, one can calculate the magnitude of the change of the refractive index. A plot of the transmission of the probing beam as a function of excitation beam intensities is shown in Fig. 11. This

Fig. 11. Transient transmission of the probing beam as a function of the nitrogen excitation power on titanium (001). (XBL 7612-7956)

result was only recently observed and consequently before any quantitative conclusions can be reached we must study the response as (i) a function of delay time of the probing beam, (ii) pH values of the electrolyte, and (iii) biasing voltage across the TiO_2 electrode and Pt electrode which pins the Fermi energy.

7. RESEARCH PLANS FOR CALENDAR YEAR 1977

C. B. Harris

a. Spectroscopy of Molecules Absorbed on Metal Surfaces. The development of surface spectroscopy for studying the changes in the electronic and molecular structure of aromatic hydrocarbons absorbed on metal surfaces will be an important objective with the 1977 program. We are studying aromatic hydrocarbons on nickel (111) and nickel

step surfaces with the objective of finding site selective transitions that can be used to identify molecules absorbed at the site selective surface states and for studying energy transfer from the molecular to the surface states.

b. Coherent Spectroscopy in Excited States. This program is well advanced now although one very important aspect needs to be developed. That is, a theoretical investigation into the coherent averaging of transitions in the optical region using variations in the wave vector as a means to control the average Hamiltonian. We will be initiating the theoretical investigations as well as preliminary experiments utilizing a tunable dye laser and picosecond sources. The idea is simply that the wave vector in a time dependent Hamiltonian for coherent coupling of an oscillating electric field in the optical regime bears a direct relationship to the phase factor in the time dependent Hamiltonian for microwave or radio-frequency sources. We would like to develop the theory for both linear and nonlinear processes.

c. Picosecond Studies of Energy Transfer Processes in Solids. Now that the instrumentation and initial experiments in the study of coherence and relaxation processes in condensed phases are near completion we will be developing an intense program into studying relaxation in condensed phase. This is an area where a great deal of theory is emerging rapidly, however, virtually no experiments have been obtained with the exception of those in the liquid phase by Kaiser and Laubereau in Munich. These are very difficult experiments but well worth pursuing because of their ability to probe the primary processes on a time scale shorter, in some instances than 10^{-12} seconds.

d. Picosecond Studies on Semiconductor Surfaces. The initial experiments using spectroscopic ellipsometry to study electron-hole recombination rates on semiconductor surfaces (see preceding article No. 6b) are very encouraging. The signal-to-noise ratio in these experiments are large and the experiments are relatively simple and straightforward to do and thus hold promise of measuring a variety of phenomena. These include (i) surface electron-hole recombination rates as a function of temperature and extrinsic P or N type character, (ii) to measure electron diffusion rates from the surface to the bulk as a function of band bending, and (iii) the study of the interrelationships of band bending to photo-electrolytic chemical processes.

e. Energy Transfer Processes of Molecular Solids. These studies are continuing however the emphasis is to transfer the theoretical basis for the experiments from the microwave region into the optical region combining what we have learned from coherent averaging in triplet states. Additionally, we will develop thermal modulation techniques to study phonon-exciton scattering in molecular and non-molecular solids.

8. 1976 PUBLICATIONS AND REPORTS

Charles B. Harris and Associates

Journals

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2. R. M. Shelby, A. H. Zewail and C. B. Harris, Coherent Energy Migration in Solids: Determination of the Average Coherence Length in One-dimensional Systems Using Tunable Dye Lasers, J. Chem. Phys. 64, 3192 (1976).
3. C. B. Harris, Coherence in ODMR: A New Tool for Spectroscopists, Electron Spin Resonance Conference Proceedings, Nijmegen, The Netherlands, August 1976.

Papers Presented

1. IBM Research Colloquium, San Jose, "Coherent Averaging Techniques in Optically Detected Magnetic Resonance."
2. Department of Chemistry, University of California, La Jolla, "Coherent Energy Migration in Solids".
3. Electron Spin Resonance Conference, Nijmegen, The Netherlands, "Coherence in ODMR: A New Tool for Spectroscopists."

4. Department of Chemistry, University of Michigan, "Optically Detected Magnetic Resonance and Coherent Spectroscopy in Excited States."

5. Wayne State University, Detroit, Michigan, "Coherent Spectroscopy and Energy Transfer Processes in Solids."

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4. A. H. Zewail, W. G. Breiland, and C. B. Harris, The Lifetimes of Translationally Equivalent Dimers and Their Relationship to the Franck-Condon Progression in the Optical Spectrum, LBL-5107, 1976.
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b. Electron Paramagnetic Resonance

Rollie J. Myers, Principal Investigator

1. HIGH-FIELD NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY ON C-13 AND OTHER NUCLEI

David J. Ruben and Rollie J. Myers

About a year ago the Department of Chemistry received a grant of over \$200 K from NSF to obtain a high-field nuclear magnetic-resonance spectrometer. After an exhaustive investigation we decided to build our own instrument but to base it on the Bruker wide-bore (180 MHz for protons) superconducting magnet. This decision was greatly influenced by the fact that we could assemble a good team for the construction and that Dr. David J. Ruben of A. Pines' group could be made available to us.

A number of MMRD investigators participated in the original proposal to NSF and it called for an instrument which could be used for a wide number of nuclei with maximum sensitivity. The Bruker magnet had been used in one previous high-resolution instrument and it had been proven that sample tubes up to 25 mm in diameter could be used for many nuclei.

For the past six months we have worked on the construction and design of the electronics and our first spectra have just been obtained. We have started out with 10 mm diam. sample tubes for protons, and outstanding resolution and sensitivity have been obtained. We are now doing proton samples on an experimental basis and by the end of January we hope to also be doing C-13 in 25 mm diam. tubes. Other nuclei will be added so that we expect to have a nearly finished machine by next July. The highly sensitive C-13 capability should allow us to do work on catalytic systems, and when we can examine nuclei such as N-15, P-31, Co-59, Rh-103, Pt-195, etc., we should have a very powerful tool.

2. ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY ON TRANSITION METAL COMPLEXES

Duane L. Lindner and Rollie J. Myers

Our work on the binuclear fulvalene complexes has been restricted to the $\text{Co}_2(\text{C}_{10}\text{H}_8)_2^+$ ion where the cobalts appear to be an equivalent pair as shown by other workers. In collaboration with Professor James C. Smart we have attempted to resolve proton hyperfine structure in addition to the 15-line pattern from the two Co-59 nuclei. A large number of solvents were tried, but so far we have only obtained a slight improvement over the spectrum obtained in dimethylformamide. We still hope to completely resolve this spectrum so that we establish the importance of the $\text{C}_{10}\text{H}_8^-$ radical anion in the electronic structure. We may attempt a nuclear polarization experiment to obtain better resolution.

Our work on ferritin has resulted in an interesting assignment for Cu^{2+} and VO^{2+} bound to this protein. We are attempting to find an

"active site" which is involved in the catalytic conversion of Fe^{2+} into Fe^{3+} . It seems very clear at this point that the Cu^{2+} site is not the same one as that which binds Fe^{2+} while the VO^{2+} does seem to correspond to this site. The most interesting feature of this VO^{2+} site is that the VO^{2+} complex has a very short correlation time for what appears to be a nearly isotropic rotation. One interpretation is that the VO^{2+} (and hence the Fe^{2+}) is bound to a site with great freedom of motion so that the complex can also be involved in transport within this very large molecule. In this way the iron could be transported from "outside" to "inside" the protein for storage as Fe^{3+} .

The nearly isotropic EPR spectrum that is observed at room temperature and in solution for the VO^{2+} complex is shown in Fig. 1.

Fig. 1. Isotropic appearance of VO^{2+} bound to ferritin.
(XBL 766-8066)

3. ELECTRON PARAMAGNETIC RESONANCE SPECTRA OF SUBSTITUTED CYCLOOCTATETRAENE RADICAL ANIONS

James H. Hammons and Rollie J. Myers

During 1974 we assigned the EPR spectra of the radical anions of several substituted cyclooctatetraene radical anions. At that time it was not possible to make a completely satisfactory explanation of the observed distribution of the odd-electron around the eight-membered ring. The reasons for this is that we did not completely understand the effects of the Jahn-Teller distortion on the odd-electron wavefunction.

We have now constructed a satisfactory mathematical model for this distortion and checked these results with INDO energy calculations. In summary, the Jahn-Teller distortion gives an alternation

in the C-C bond lengths around the ring. With this alternation all the carbon atoms remain equivalent. However, the effect of a substitution is to destroy this equivalence and thus to oppose the Jahn-Teller distortion. The resulting distortion is a compromise between these two factors. With a CH₃ substitution the lowest energy still has a bond length alternation, but with an F substitution the lowest energy form seems to have equal bond lengths.

While this model gives a very satisfactory fit to the observed splittings at one temperature it does not completely explain the small observed changes with temperature. One limitation in our model is that it completely neglects a second kind of Jahn-Teller distortion involving the C-C-C bond angles. It seems very likely that for an F substitution the primary distortion is of this second kind. In this way, the Jahn-Teller distortion problem becomes that of a two-dimensional potential energy surface, and temperature can change the distribution of the molecules on this surface.

4. RESEARCH PLANS FOR CALENDAR YEAR 1977

Rollie J. Myers

Now that the high-field nuclear magnetic resonance spectrometer is operational we plan to use this tool for a study of systems of importance for chemical catalysis. This technique requires that samples be in solution. While this would restrict us to bulk sampling techniques for heterogeneous catalysis, it will allow us to directly study homogeneous catalysis. The large sample size of this new spectrometer will give relatively high sensitivity for nuclear magnetic resonance. For protons it should be possible to detect and characterize products in solution whose concentration is less than 10⁻⁵%. This corresponds to a 10⁻⁴ M solution if the molecular weight were 100. Such concentrations are the expected levels of many of the intermediates in chemical reactions. The major advantage of high resolution NMR is that the observed chemical shifts and resolved spin-spin splittings can also be used to

characterize functional groups and to establish molecular structures.

Since this spectrometer can also be used for a wide variety of nuclei in addition to protons, we also plan to follow, for example, a sample of C-13 enriched carbon monoxide when it is introduced into a system which can catalytically reduce it. In addition to C-13 it should also be possible to follow Rh-103, or Pt-195, for example, and to characterize the dynamic complexes which they can form.

In some catalytic systems the transition-metal ions form a variety of paramagnetic complexes. For these cases we should either observe enhanced nuclear relaxation or even electron paramagnetic resonance spectra. A particular interesting possibility is that of observing dynamic nuclear polarization with our high-power DNP spectrometer. In this way it could be possible to further identify the paramagnetic intermediates which may be present in catalytic systems.

In addition to our work on catalytic systems we will also use both the new NMR and our old EPR spectrometers to study interesting problems in molecular structural studies. Examples of these would be our substituted cyclooctatetraene radical anions and certain first-row transition metal complexes.

5. 1976 PUBLICATIONS AND REPORTS

Rollie J. Myers and Associates

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1. Michael R. St. John and Rollie J. Myers, Electron-Paramagnetic-Resonance Spectra of Ions substituted into Transition-Metal Ion Lattices, Phys. Rev. B 13, 1006 (1976) (LBL-4189).
2. Richard C. Wilson and Rollie J. Myers, Electron-Paramagnetic-Resonance Spectrum and Spin Relaxation for Ti(H₂O)₆³⁺ in Aqueous Solution and in Frozen Glass, J. Chem. Phys. 64, 2208 (1976) (LBL-4165).

c. Physical Chemistry with Emphasis on Thermodynamic Properties

Kenneth S. Pitzer, Principal Investigator

1. QUANTUM CHEMISTRY FOR HEAVY ATOMS

Kenneth S. Pitzer, Walter C. Ermler, and Yoon S. Lee

The purely exploratory calculations, which showed the importance of relativistic effects and were reported last year, have now been published in three short notes. Our recent work has been directed toward a pseudo-potential or effective-potential method, based upon relativistic calculations for individual heavy atoms, but otherwise following the promising path of recent work of Goddard,¹ Kahn,² and others for lighter atoms where relativistic effects may be ignored. The relativistic terms are most important near the center of an atom; hence, they will have a substantial effect on each pseudo-potential. And for p electrons there will be a finite difference in wavefunction and pseudo-potential for $p_{1/2}$ as compared to $p_{3/2}$ orbitals (also $d_{3/2}$ and $d_{5/2}$ orbitals, etc.). While these effects will add some complication to molecular calculations, they should be tractable.

The fully relativistic (Dirac) theory, however, has many more complications which would make molecular calculations very difficult, and we must learn whether any or all of these features may be neglected in satisfactory approximation for the valence shell electrons. In particular Dirac atomic functions are not scalars but have four components:

$$\psi_{nk} = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} = \frac{1}{r} \begin{pmatrix} P_{nk}(r) \chi_{km}(\theta, \phi) \\ iQ_{nk}(r) \chi_{-km}(\theta, \phi) \end{pmatrix} \quad (1)$$

where

$$\chi_{km}(\theta, \phi) = \sum_{\sigma=\pm 1/2} C Y^{m-\sigma}(\theta, \phi) \Phi_{1/2}^{\sigma},$$

Y is a spherical harmonic,

$$\Phi_{1/2}^{1/2} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \Phi_{1/2}^{-1/2} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

C is a Clebsch-Gordan coefficient,

$$\lambda = k = (j + \frac{1}{2})$$

if $j = \ell - 1/2$ and $\lambda = -(k+1) = (j + \frac{1}{2})$ if $j = \ell + \frac{1}{2}$.

In Eq. (1) k is the relativistic quantum number. P_{nk} and Q_{nk} satisfy the following coupled equations when V is a potential in the central field.

$$\begin{aligned} \frac{dP_{nk}}{dr} + \frac{kP_{nk}}{r} - (2/\alpha + \alpha[V - E_{nk}]) Q_{nk} &= 0 \\ \frac{dQ_{nk}}{dr} - \frac{kQ_{nk}}{r} + \alpha(V - E_{nk}) P_{nk} &= 0 \end{aligned} \quad (2)$$

Atomic units are used in Eq. (2) and all the following expressions.

In the nonrelativistic limit, the "small" component Q_{nk} becomes completely negligible compared to the large component P_{nk} . Also in this limit the two, coupled first order Eq. (2) reduce to a single, second order equation which is the familiar Schrödinger equation.

Thus it becomes important to follow the magnitude of the small component, both in the original Dirac-Fock wave functions for valence-shell electrons in heavy atoms and in the transformed pseudo-functions for these same electrons.

Once the integrations with respect to angular variable have been carried out, the electron density is given by

$$\psi_{nk}^2 = P_{nk}^2 + Q_{nk}^2 \quad (3)$$

Hence our concern is whether Q^2 is negligible as compared to P^2 . For heavy atoms such as Pb or U, the ratio of Q^2 to P^2 varies greatly for different orbitals or for different radii for a valence-shell orbital. It is by no means negligible for 1s or other inner shell orbitals. Indeed for U the ratio of radially integrated densities is below 10^{-4} only for the 6d and 7s orbitals; it is about 10^{-3} for 5s and 5p orbitals.

The radial variation of P and Q is shown in Fig. 1 for a 6s electron in bismuth; note the ten-fold expansion by plotting $10Q$. While Q is evidently negligible as compared to P in the outer portion of the atom, it is not negligible near the nucleus.

In the formation of pseudo-orbitals a linear combination of orbitals of the same angular symmetry is chosen that eliminates the radial nodes yet leaves essentially the original valence-shell function in the outer portion of the atom. When this is done for the 6s orbital of bismuth the result is shown in Fig. 2. Here one sees that the small component Q is now very small and presumably negligible in the inner as well as in the outer part of the atom.

While we still have to examine many points in greater detail, the above results, and others like them, indicate that a pseudo-potential approach should be feasible and that one will be able to use a nonrelativistic Hamiltonian in calculations with pseudo-potentials and pseudo-orbitals.

Fig. 1. The large and small components, P and Q, for the 6s orbital in bismuth. Note that the curve shows 10Q. (XBL 7612-10944)

Fig. 2. The large and small components, P and Q, for a pseudo-orbital for a 6s electron in bismuth. Note that the curve shows 10Q. (XBL 7612-10945)

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2. L. R. Kahn, P. Baybutt, and D. G. Truhlar, J. Chem. Phys. 65, 3826 (1976).

2. SOLUTIONS OF ELECTROLYTES AT HIGH TEMPERATURES

Kenneth S. Pitzer, Leonard F. Silvester, and Pamela Z. Rogers

The development of equations for the enthalpy, heat capacity, and activity, and osmotic coefficients for aqueous sodium chloride at saturation pressure (or 1 atm) up to 300°C was

completed and reported. For the osmotic coefficient the equation is

$$\phi - 1 = -A_{\phi} \frac{m^{1/2}}{1 + bm^{1/2}} + m(\beta^{(1)} + \beta^{(1)} e^{-\alpha m^{1/2}}) + m^2 C^{\phi} \quad (1)$$

where A_{ϕ} is the Debye-Hückel coefficient, b and α are general parameters assigned the values 1.2 and 2.0, respectively, and $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} are parameters specific to the solute, NaCl in this case. All except b and α are temperature dependent. A_{ϕ} is given by solvent properties while $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} must be evaluated from data for sodium chloride over a range of temperature.

Equations for the other quantities follow from thermodynamics. In particular the enthalpy involves the temperature derivatives of A_{ϕ} , $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} while the heat capacity requires also the second temperature derivatives of these parameters.

This equation reproduced the osmotic data to ± 0.005 for compositions from 0 to 6 M and from 0 to 300°C, enthalpy data to ± 5 to 10 cal/mole for compositions to 5 M and from 28 to 100°C, and heat capacity data to ± 0.5 cal/degree mole for compositions to 2 M from 25 to 200°C.

Work is now underway on the representation of volumetric data for sodium chloride with the further objective of calculating thermodynamic properties at pressures above that of the saturated vapor.

In addition to the theoretical and modeling program, an experimental program was initiated which involves the design and construction of a densimeter and calorimeter for aqueous electrolytes to 700 bars and 300°C. The calorimeter is discussed more fully in our report for the Geoscience program which provided the primary support. This experimental program has two goals: (1) to supply data on simple and complex electrolyte systems which have not been measured in this domain; and (2) to provide data for checking and refining various theoretical equations and models.

3. THERMODYNAMIC PROPERTIES OF SULFURIC ACID

Kenneth S. Pitzer, Rabindra N. Roy, and Leonard F. Silvester

Our equations for the thermodynamics of strong electrolytes which are theoretically based but adapted for convenient and accurate representation of experimental data to high concentration were extended last year for a simple weak electrolyte. They were applied, as an example, to pure phosphoric acid and to phosphate buffers. We have now extended this program to the extremely important case of sulfuric acid. Solutions of this acid are especially difficult to treat because the partial dissociation of the HSO_4^- ion has a low pK and yields the divalent SO_4^{2-} .

The experimental properties of solutions above 0.1 M at 25°C are well established.¹ Below 0.1 M there are fewer experimental studies of high accuracy and there is some disagreement. The most unambiguously interpretable data for the dilute range are those of Shrawder and Cowperthwaite² for the cell $\text{Pt}, \text{H}_2/\text{H}_2\text{SO}_4(\text{m})/\text{PbSO}_4, \text{Pb}, \text{Hg}$ with m ranging from 0.001 to 0.02 M and at temperatures from 0 to 50°C. Surprisingly, these data had never been interpreted in a straightforward manner with appropriate theory but without use of other information of doubtful validity. As a preliminary step in our work on sulfuric acid these data were fitted to the very simple equations appropriate to this dilute range and the dissociation constant for HSO_4^- was determined. This preliminary study has been completed and submitted for publication.

Calculations covering the full range of concentration up to 6 M and for the enthalpy as well as the activity and osmotic coefficients are progressing well but are not yet complete. They do show, however, that the data of Shrawder and Cowperthwaite in the range below 0.1 M are fully compatible with the activity coefficient data above 0.1 M.

1. For example, see J. A. Duisman and W. F. Giaque, *J. Phys. Chem.* **72**, 562 (1968).
2. J. Shrawder and I. A. Cowperthwaite, *J. Am. Chem. Soc.* **56**, 2340 (1934).

4. RESEARCH PLANS FOR CALENDAR YEAR 1977

Kenneth S. Pitzer

The development of a quantum chemistry for heavy atoms will continue toward more detailed and quantitative calculations. Since we now have reasonable assurance that a pseudo-potential approach can be successful, even when relativistic effects are significant, we will proceed to evaluate the numerical pseudo-potentials and pseudo-orbitals for several heavy atoms of chemical interest and then to obtain more convenient expressions, probably as sums of Gaussian functions. Initial applications will include species such as Bi^+ which are anomalous in terms of periodic table trends from lighter elements.

The work on the thermodynamics of electrolytes (assisted also by the Geoscience program) will emphasize both experimental (calorimetric) measurements and theoretical treatments related to the high-temperature and high-pressure properties of pure electrolytes which are important components in geochemical and geothermal brines. We believe that our present

equations for mixed electrolytes will be valid in this new domain, but it will be desirable to make some measurements on mixtures after the work on their pure components has been completed.

Information about thermodynamic properties of electrolytes over a range of temperature should make it possible to draw further conclusions about the short-range forces between ions (in the presence of the solvent), but this work will probably not be significant until 1978 or later.

5. 1976 PUBLICATIONS AND REPORTS

Kenneth S. Pitzer and Associates

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* Major support not supported by ERDA.

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3. Janice J. Kim and Kenneth S. Pitzer, Crystal Field Effects on Oxygen in Solid Methane and the Catalysis of Spin-Species Conversion of Methane, LBL-5476, September 1976, submitted to *J. Chem. Phys.*

d. Chemical Dynamics Studies

Bruce H. Mahan, Principal Investigator

1. SEQUENTIAL IMPULSE MODEL OF DIRECT REACTIONS*

Bruce H. Mahan, Walter E. Ruska, and John S. Winn

During the last three years, we have been developing a model for predicting the angular and energy distributions of products of reactions carried out at energies which are large compared with the dissociation energy of chemical bonds.¹ The general reaction $A(BC,C)AB$ is viewed as the result of two hard sphere elastic impulses between the A-B and B-C atom pairs. In the initial formulation of the model, product energy and angular distributions were computed by numerically calculating the final states which result from an appropriately weighted set of initial conditions. These "trajectory" calculations could be done extremely rapidly and economically because of the simple intermolecular potential assumed in the model. A comparison of the calculated distributions with those obtained from experiments on the $O^+(H_2,H)OH^+$ system yielded very encouraging results.

In the past year, we have completed an analytical treatment of the sequential impulse model. A compact, easy to evaluate expression for the product velocity vector distribution has been obtained which reproduces the results obtained earlier by numerical methods. However, the analytical expression provides much more detail with essentially no calculational effort, and directly displays the factors which influence the reaction cross section and product velocity vector distribution. The total reaction cross section is most sensitive to the hard sphere diameters of atoms A and B and total collision energy, and is relatively insensitive to other parameters. The ratio of product at the spectator stripping velocity to that scattered through large angles is sensitive to the ratio of the mutual hard sphere diameter of atoms B and C to the equilibrium bond distance of the BC molecule. The detailed shape of the large angle scattering is relatively insensitive to the total energy or the parameters of the potential. The angular distribution of products is very sensitive to the mass ratio of atoms B and C, and much less sensitive to their absolute masses if these are small compared with the mass of atom A. All these predictions of the model have been recognized in experimental results,^{1,2} and it is anticipated that the model can be used to predict the behavior of systems which are difficult to investigate experimentally.

2. HIGH ENERGY REACTIVE SCATTERING OF N^+ by H_2 *

Bruce H. Mahan and Walter E. Ruska

Product velocity vector distributions have been measured for the reaction $N^+(H_2,H)NH^+$ and its isotopic variants in the range of relative energies above 6 eV. Despite the existence of a deep potential energy well corresponding to NH_2^+ , at high energies the system follows potential energy surfaces which are relatively flat along the reaction coordinate. As a result, the reaction is expected to follow a direct interaction mechanism, and experiments show that this is in fact the case.

The reaction $N^+(H_2,H)NH^+$ is thermoneutral within experimental uncertainty when reactions and products are in their ground electronic states. Thus in the high relative energy range, its dynamics should be described accurately by the sequential impulse model of direct reactions.^{1,2} This model predicts that at initial relative energies at which product formed by spectator stripping is stable with respect to dissociation, it will be the most prominent feature of the distribution. In reactions of N^+ with HD, the NH^+ distribution will retain the spectator stripping feature and be predominately forward scattered at energies at which ND^+ can not be formed by spectator stripping and will be predominantly backward scattered.

Figures 1 and 2 show the distributions of NH^+ and ND^+ respectively from N^+ -HD collisions at an initial relative energy of 9.7 eV. The results are generally consistent with the predictions of the sequential impulse model. At this relative energy, NH^+ formed by spectator stripping is stable with respect to dissociation, there is a peak at the spectator stripping velocity, and the NH^+ product is generally forward scattered. In contrast, there is very little ND^+ product at angles less than 90° , and most of the intensity is concentrated in the angular range near 180° . The fairly pronounced peak at 180° is not anticipated by the sequential impulse model, and evidently is a consequence of angular terms in the potential energy which are ignored in the sequential impulse model.

* Abstracted from LBL-5197, and a paper to be published in the J. of Chem. Phys.

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* Abstracted from LBL-5454 and a paper to be published in the J. of Chem. Phys.

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Fig. 1. A contour map of the specific intensity of NH^+ from the $\text{N}^+(\text{HD},\text{D})\text{NH}^+$ reaction at 9.7 eV initial relative energy. The small cross marks the spectator stripping velocity. The circles labeled $Q = -4.6$ and $Q = 0.6$ define the velocity range in which stable product is expected.

(XBL 771-7400)

Fig. 2. A contour map of the specific intensity of ND^+ from the $\text{N}^+(\text{HD},\text{H})\text{ND}^+$ reaction at 9.7 eV initial relative energy.

(XBL 771-7401)

3. LOW ENERGY REACTIVE SCATTERING OF N^+ BY H_2 *

James M. Farrar, Steven G. Hansen, and Bruce H. Mahan

The reaction $\text{N}^+(\text{H}_2,\text{H})\text{NH}^+$ has been investigated in our laboratory in the high,¹ intermediate,² and

low³ ranges of initial relative energy. The reaction is particularly interesting in that the ground-state reactants can approach each other on one of three different potential energy surfaces.^{1,3} Only one of these provides a low energy path from reactants to the deep ground-state potential energy well of the NH_2^+ intermediate, and from there to products. However, this potential energy well is accessible only if the collision geometry is intermediate between collinear NHH^+ and the isosceles triangle (C_{2v}) conformations. These conclusions, which were reached by a correlation diagram analysis of the system,³ have recently been confirmed by *ab initio* calculations of Schaefer and co-workers,⁴ and Gittins and Hirst.⁵

Fair and Mahan³ found sufficient symmetry in the NH^+ product velocity vector distribution at a relative energy of 0.79 eV to conclude that the potential well of NH_2^+ is in fact accessible to reactants in low energy collisions. However, the resolution of the experiment was limited by their use of a scattering cell to contain the H_2 target gas. We have reinvestigated the reaction at low energies, taking advantage of the increased resolution of our new low energy ion-crossed molecular beam apparatus.

Figure 1 shows some typical results for the product distributions at low relative energies. The distribution of Fig. 1a was obtained with N^+ prepared by high energy electron impact on N_2 . It consists of two components, one symmetric about and peaked at the centroid velocity, and the other peaked in the small angle scattering region. Figure 1b shows the distribution obtained when N^+ is prepared by a microwave discharge through N_2 , a method which produces only ground state (^3P) N^+ . There is only one feature to this distribution. The approximate symmetry about the centroid velocity shows that ground state N^+ does react with H_2 to form a long lived NH_2^+ complex which dissociates to products only after several rotations. The fact that two features appear in Fig. 1a indicates that N^+ beams prepared by high energy electron impact contain, in addition to $\text{N}^+(^3\text{P})$, significant quantities of metastable excited N^+ , probably $\text{N}^+(^1\text{D})$. The correlation diagram³ for this system shows that $\text{N}^+(^1\text{D})$ should react with H_2 by a short-lived direct interaction, and produce a peak in the small angle region. Thus the increased resolution of our new apparatus has led to the confirmation of our conclusion concerning the reaction of ground state N^+ , and revealed new information concerning the reaction of the metastable excited state.

* Abstracted from J. Chem. Phys. **65**, 1956 (1976) and LBL-5400.

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Fig. 1. Contour maps of the specific intensity of NH^+ . (a) Projectile ions from 160 eV electron impact on N_2 . (b) Ground-state projectile ions drawn from a microwave discharge through N_2 . For clarity, the beam profiles have been displaced from their true positions (located by dots and 0°). (XBL 771-7402)

4. A LOW ENERGY ION-MOLECULAR BEAM APPARATUS

James M. Farrar

We have completed the design and construction of an apparatus which permits the measurement of the energy and angular distributions of the products of ion-molecule reactions carried out at low relative kinetic energy. The apparatus consists of a high intensity electron impact ion source followed by a magnetic mass spectrometer and ion decelerator which produces a collimated ion beam of 0.5-10 eV laboratory energy with a space charge limited intensity. This ion beam crosses a neutral molecular beam which is formed by mass flow through a small pinhole. The detector train is mounted on a rotatable lid of the vacuum chamber, and consists of a 90° electrostatic ion energy analyzer, a quadrupole

mass spectrometer, an ion to electron converter, and a scintillation electron counter. The entire ion path is constructed so as to maintain clean surfaces and prevent surface charge build up which might destroy the quality of the beam. In addition, differential pumping of the source and detector regions is employed to diminish the importance of reactions of beam ions with background gas. The apparatus has performed very well and has produced stable beams of N_2^+ , N^+ , and F^+ with laboratory energies as low as 1 eV. The apparatus has been used to study the reactions $N^+(H_2,H)NH^+$ and $F^+(H_2,H)HF^+$, and has revealed new aspects of both systems.

* Abstracted from LBL-5478.

5. DYNAMICS OF THE F^+-H_2 REACTION

James M. Farrar, Steven G. Hansen, and Bruce H. Mahan

The reaction $F^+(H_2,H)HF^+$ is particularly interesting in that the reactants F^+ and H_2 constitute an excited state of the system which does not correlate adiabatically to known bound states of HF^+ . Nevertheless, HF^+ is observed as a product, and must be formed by a process which involves an electronic transition from one surface to another. The correlation diagram analysis of the system suggests that such transitions may occur in regions where two or more potential energy surfaces are in proximity. However, because of the density of electronic surfaces and the uncertainty about the details of their positions and shapes, it is difficult to specify the nature of the transitions that lead from reactants to products.

Our experiments show that the energy and angular distribution of HF^+ is sensitive to the source of F^+ and to the initial relative energy. When F^+ is formed by high energy electron impact on NF_3 , an asymmetric product distribution is found which indicates that the reaction proceeds by a direct interaction mechanism. When F^+ is obtained by high energy electron impact on a fluorocarbon, a component symmetric about the centroid velocity is added to the distribution, if the initial relative collision energy is in the range of 0.3 to 0.7 eV. This suggests that metastable excited states of F^+ may, at appropriate initial relative energies, be forming product by a process which involves a long-lived collision intermediate. This problem is being pursued from both experimental and theoretical approaches.

6. LASER INDUCED FLUORESCENCE OF GASEOUS IONS

Richard Davis, Frederick Grieman, and Bruce H. Mahan

We have constructed an apparatus for the purpose of obtaining the electronic spectra of small gaseous ions. The ions are formed by

electron impact, trapped mass selectively by a radiofrequency quadrupole mass spectrometer, irradiated by the light from a tunable dye laser, and any fluorescence detected by a photo-multiplier. Preliminary experiments with the first version of this apparatus showed that it was possible to trap ions in sufficient quantities to obtain their fluorescent spectra, but that scattered light from the laser optical path made detection difficult or impossible. The apparatus is being modified in order to diminish scattered laser light, and increase the number of ions in the irradiated portion of the trap. Initial experiments with the modified apparatus should begin early in 1977.

7. RESEARCH PLANS FOR CALENDAR YEAR 1977

Bruce H. Mahan

We will continue our tests of the sequential impulse model by studying the high energy scattering of C^+ and Cl^+ by H_2 . The connection between electronic structure and chemical reactivity will be extended by completing the work on the low energy scattering of F^+ by H_2 , and by examining the reactions of CF^+ , S^+ , and P^+ with H_2 at low energies. A doubly differentially pumped molecular beam source will be added to our low energy apparatus in order to facilitate the study of nonreactive energy transfer processes. The modifications on the laser induced fluorescence apparatus will be completed and the study of gaseous ion spectra begun.

8. 1976 PUBLICATIONS AND REPORTS

Bruce H. Mahan and Associates

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e. Theory of Low Energy Atomic and Molecular Collisions

William H. Miller, Principal Investigator

1. SEMICLASSICAL THEORY FOR EIGENVALUES AND REACTION RATE CONSTANTS OF NON-SEPARABLE SYSTEMS*

William H. Miller

Considerable progress has been made in the development and application of semiclassical theory based on solution of the classical Hamilton-Jacobi equation of the dynamical system in question. The fact which has made this possible is that ways have been found¹ for constructing the classical Hamiltonian of a non-separable system in terms of its complete set of "good" action-angle variables.

The vibrational energy levels of a triatomic molecule present a good example for application of this theory. The usual normal mode approximation is inadequate for high vibrational states, and perturbation theory is often not sufficient to deal with the non-separable interactions. The energy levels are obtained semiclassically by expressing the classical Hamiltonian in terms of the "good" action variables and requiring them to be integral. Calculations based on the methods of Chapman, Garrett and Miller¹ have been carried out (with good results) for vibrational states of H₂O and SO₂² and further development of the methodology is being vigorously pursued by other workers.³

The Hamilton-Jacobi formalism can also be applied to the recently formulated quantum mechanical extension of transition-state theory⁴ that takes the non-separability of the transition-state region into account. This results in a semiclassical limit of quantum mechanical transition-state theory which is seen to have a number of illuminating features in common with more conventional transition state theory.

More specifically, the rate constant for a bimolecular reaction can be expressed as

$$k(T) = (2\pi h Q_R)^{-1} \int dE e^{-E/kT} N(E), \quad (1)$$

where Q_R is the partition function per unit volume for the reactants and E is the total energy. The expression for $N(E)$ in conventional transition state theory is

$$N(E) = \sum_{n_1, n_2, \dots, n_{F-1}} P(E - \epsilon_{n_1, n_2, \dots, n_{F-1}}), \quad (2)$$

where $\{\epsilon\}$ are the energy levels of the $F-1$ degrees of freedom of the activated complex, and $P(E_F)$ is the one-dimensional tunneling probability for the F^{th} degree of freedom (the reaction coordinate) with an energy E_F in it. The expression which results from the Hamilton-Jacobi version of the generalized transition state theory is

$$N(E) = \sum_{n_1, n_2, \dots, n_{F-1}} [1 + e^{2\pi i \text{Im } n_F(n_1, n_2, \dots, n_{F-1}, E)}]^{-1}, \quad (3)$$

where $E(n_1, \dots, n_F)$ is the total (non-separable) Hamiltonian as a function of its complete set of "good" action angle variables. In Eq. (3), however, one needs n_F , the action-variable associated with the reaction coordinate, expressed in terms of E and all the other actions; i.e., one must solve the equation

$$E(n_1, n_2, \dots, n_{F-1}, n_F) = E \quad (4)$$

for $n_F(n_1, \dots, n_{F-1}, E)$. Since the reaction coordinates sees a potential barrier, rather than a potential well, this action variable is in general complex, and its imaginary part provides a semiclassical approximation to the tunneling probability. The important feature is that although Eq. (3) entails a semiclassical approximation, it does not require the assumption of separability of the Hamiltonian in the transition state region.

* Abstracted from *The New World of Quantum Chemistry*, Eds. B. Pullman and R. Parr, Reidel Publishing Company, Dordrecht (Netherlands) 1976, and Faraday Discussions Chemical Society 62, 87 (1976).

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2. SEMICLASSICAL EIGENVALUES FOR IRREGULAR SPECTRA*

William H. Miller

The Hamilton-Jacobi approach¹ to determining the semiclassical eigenvalues of a non-separable system can be successful only if a complete set of good action variables exists. This may not always be the case, i.e., the spectrum of eigenvalues may be irregular. None of the previously known semiclassical approaches can deal (or even make sense) with the case of an irregular spectrum.

By invoking a different ansatz for the relevant generating function, however, it is possible to obtain a semiclassical eigenvalue equation that does not explicitly require the existence of a

complete set of good action variables. This equation thus permits one to define semiclassical eigenvalues without reference to a complete set of good action variables and thus has possible application to the case of irregular spectra.

The key idea is recognizing that semiclassical quantization results in Hamilton-Jacobi theory because the generating function is required to be the logarithm of a periodic function of the "old" angle variables. (This is essentially the requirement that the wavefunction be single-valued in physical space.) One thus takes the generating function $F(q)$ as the logarithm of a Fourier series,

$$F(q) = -i \ln \left[\sum_{\underline{k}} c_{\underline{k}} e^{i \underline{k} \cdot \underline{q}} \right], \quad (1)$$

and substitutes this form for $F(q)$ into the Hamilton-Jacobi equation:

$$\omega \cdot \frac{\partial F(q)}{\partial \underline{q}} + V(q, \frac{\partial F}{\partial \underline{q}}) = E. \quad (2)$$

Straightforward manipulations then lead to the following secular equation

$$\det |\omega \cdot \underline{k} \delta_{\underline{k}, \underline{k}'} + V_{\underline{k}, \underline{k}'} - E \delta_{\underline{k}, \underline{k}'}| = 0, \quad (3)$$

where

$$V_{\underline{k}, \underline{k}'} = (2\pi)^{-F} \int_0^{2\pi} d\underline{q} e^{-i(\underline{k}-\underline{k}') \cdot \underline{q}} V(\underline{q}, \underline{n}(\underline{q})), \quad (4)$$

with

$$\underline{n}(\underline{q}) = \frac{\sum_{\underline{k}} \underline{k} c_{\underline{k}} e^{i \underline{k} \cdot \underline{q}}}{\sum_{\underline{k}} c_{\underline{k}} e^{i \underline{k} \cdot \underline{q}}} \quad (5)$$

It is clear that Eq. (3) leads to discrete eigenvalues for E , for the same reasons that secular equations do in quantum mechanics, but this is still strictly within the framework of classical mechanics. Quantization of energy has resulted because of the boundary conditions imposed on the generating function. This procedure does not construct the Hamiltonian as a function of a complete set of good action variables, which are *ex post facto* required to be integers. Rather it imposes the quantization boundary conditions right from the beginning and avoids the necessity of finding a complete set of good action variables, so that it is not necessary that they exist. This formulation of the semiclassical eigenvalue problem is the only existing one that does not require the existence of a complete set of good action variables.

* Abstracted from J. Chem. Phys. 64, 2880 (1976). (Supported in part by the National Science Foundation.)

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3. ATOMIC SCATTERING FROM A SINUSOIDAL HARDWALL SURFACE*

R. I. Masel,[†] R. P. Merrill,[†] and W. H. Miller

Several approximate procedures for the calculation of intensities of atoms elastically scattered from solids have been compared with exact quantum mechanical calculations that we have carried out for a sinusoidal hardwall potential. The quasiclassical method--a completely classical model--reproduces the qualitative features of the "rainbow" envelope of the scattered intensities but it does not, of course, contain any of the rich quantum interference structure in the intensities of individual diffraction orders. A popular approximate quantum theory, the CCGM method¹ which is a unitarized Born approximation, predicts only specular scattering independent of the "roughness" of the corrugated surface and is thus completely inadequate.

The semiclassical theory² that we have developed gives excellent agreement (within 2-3%) with the numerically exact quantum mechanical calculations for a wide range of "roughness". This test shows the semiclassical approximation to be the only current model capable of this kind of accuracy, and its other strength is that it can be applied to more realistic, i.e., smooth, potential models.

* Abstracted from J. Vac. Sci. Tech. 13, 355 (1976) and J. Chem. Phys. 65, 2690 (1976). (Supported in part by the National Science Foundation.)

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4. UNIFIED STATISTICAL MODEL FOR 'COMPLEX' AND 'DIRECT' REACTION MECHANISMS*

William H. Miller

The essential assumption in the conventional transition state theory for a bimolecular chemical reaction is that the reaction mechanism is *direct*, i.e., that there exists a surface that separates reactants and products which no trajectory crosses more than once. For reactions with a single activation barrier separating reactants and products this assumption of "direct" dynamics is good for collision energies not too high, so that conventional transition state theory works well for this kind of reaction.

All reactions are not "direct," however; many of them form long-lived collision complexes, and

It has also been shown that use of a variational principle to locate the relevant "dividing surfaces" through which the various fluxes in Eq. (3) are computed allows collision complexes

to exist--in the sense that there is a local maximum in the flux--even on potential energy surfaces that have no well, for example, the adiabatic trapping phenomenon and the orbiting model. Together with the variational principle for locating the dividing surfaces, the unified statistical model is thus able to describe a wide variety of different dynamical situations.

* Abstracted from J. Chem. Phys. 65, 2216 (1976).
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5. PENNING IONIZATION OF H_2 BY $He^*(2^3S)$ *

A. P. Hickman, A. D. Isaacson, and W. H. Miller

The excitation energy of the 2^3S metastable state of helium, ~ 20 eV, is sufficient to ionize any atom or molecule other than helium or neon. With H_2 the various possibilities are

which are referred to as Penning ionization (PI), associative ionization (AI), and reactive ionization (RI). These processes can be accurately described within a Born-Oppenheimer approximation, and this requires knowledge of the potential energy surface for the He^*-H_2 system, the HeH_2^+ system, and also the ionization rate as a function of nuclear positions. These calculations have been carried out, as well as preliminary calculations for the total ionization cross section.

Figure 1 shows the coordinate system for the H-H-He system. For these first calculations the H-H distance r is frozen at the equilibrium value for H_2 ; sample calculations varying r show

Fig. 1. Coordinates (R, r, θ) specifying the configuration of $He(2^3S)-H_2$. (XBL 769-4803)

negligible effect. Figure 2 shows the potential surface for He^*-H_2 in the form of the usual Legendre expansion

$$V^*(R, \theta) = \sum_{\ell=0} V_{\ell}(R) P_{\ell}(\cos \theta); \quad (2)$$

as expected, the interaction of He^* with closed shell H_2 is basically repulsive. Figure 3 shows

Fig. 2. Legendre moments $V_{\lambda}(R)$, $\lambda = 0, 2, 4$, for the $He(2^3S)-H_2$ potential energy surface (with r , the H_2 bond length, fixed at its equilibrium value $1.4 a_0$). (XBL 769-4805)

Fig. 3. Legendre moments Γ_{λ} , $\lambda = 0, 2$, of the autoionization width for $He(2^3S)-H_2$ (with the H_2 bond length fixed at its equilibrium value). (XBL 769-4806)

the width function $\Gamma(R, \theta)$ (the autoionization rate is Γ/h), also as a Legendre expansion

$$\Gamma(R, \theta) = \sum_{\ell=0} \Gamma_{\ell}(R) P_{\ell}(\cos \theta) \quad (3)$$

Γ is seen to be approximately an exponential function of R , which is expected since here autoionization is via an electron exchange process.

Quantum mechanical scattering calculations have been carried out within the framework of an optical model; i.e., the collision of He^* and H_2 is assumed to occur with the complex potential function

$$V^*(R, \theta) = \frac{i}{2} \Gamma(R, \theta) \quad (4)$$

The results of such calculations allow one to construct differential and total cross sections for non-ionizing He^*-H_2 processes--i.e., elastic scattering and rotational excitation of H_2 --and also the total cross section for ionization.

Figure 4 shows the differential cross section for un-ionized He^* . The upper curve is the result obtained if only the real part of the potential

Fig. 4. Differential elastic scattering cross sections for $\text{He}(2^3\text{S}) + \text{H}_2$ at (c.m.) collision energy $E = 0.100$ eV, assuming the initial and final rotational states of H_2 are $j=0$. The upper curve was calculated with V^* alone, while the lower curve was calculated with $V^* - i/2 \Gamma$. The cusp at $\theta = 20^\circ$ is due to the change in the horizontal scale. (XBL 769-4807)

is used; the imaginary part of the potential is thus seen to cause depletion of metastables at wide angles.

The total ionization cross section is a strongly increasing function of collision energy, being $0.10 \text{ \AA}^2$, $1.8 \text{ \AA}^2$, and $11 \text{ \AA}^2$ at translational energies of 0.01 eV, 0.1 eV, and 0.5 eV, respectively. The rate constant for ionization is a Boltzmann average over translational energy, and this is shown in Fig. 5 as a function of temperature. Experimental points are also shown, and the agreement with this completely *ab initio* theoretical calculation is seen to be quite reasonable.

Fig. 5. Rate constants for the ionization of H_2 by $\text{He}(2^3\text{S})$. The present *ab initio* theoretical results (solid curve) are compared with the experimental values obtained by Lindinger et al. (XBL 769-4808)

* Abstracted from LBL-5483 and LBL-5484. (Supported in part by the National Science Foundation.)

6. RESEARCH PLANS FOR CALENDAR YEAR 1977

William H. Miller

The collision of metastable rare gas atoms with halogen molecules--for example,

--has attracted considerable attention recently because the product molecule XeBr^* --which is essentially the ionic state Xe^+Br^- --radiates electronically to its ground repulsive state,

in laser fashion.

As a first step toward studying these processes theoretically we plan to consider collisions of metastable helium, $\text{He}(2^3\text{S})$, with fluorine atoms. Since the excitation of helium (~ 20 eV) is greater than the ionization potential of fluorine (~ 17 eV), Penning ionization can occur,

The potential curve of $\text{He}^*\text{-F}$, which is expected to be much like that of Li-F , should have an attractive well ~ 6 eV deep; this means that the $\text{He}^*\text{-F}$ potential curve will dip below that of He-F^+ for small internuclear distances and thus prohibit Penning ionization. We thus expect the Penning ionization cross section to be anomalously small in this case and to perhaps display other special features. At the next stage we plan to look at $\text{He}^* + \text{F}_2$ which can also Penning ionize, but for the same reason as for $\text{He}^* + \text{F}$ the cross section for ionization is expected to be small. There may thus be an appreciable cross section for forming the reactive produce $\text{He}^*\text{-F} \equiv \text{He}^+ \text{F}^-$ which can lase to the ground repulsive state $\text{He} + \text{F}$. This laser would be in the far UV, with $h\nu \approx 14$ eV, i.e., ~ 1200 Å photons.

Another project involving nonadiabatic collision phenomena is the chemiionization of alkaline atoms by vibrationally excited nitrogen,

Experimental measurements have obtained sizeable cross sections for this process, which indicates that a curve crossing mechanism is probably operative. We plan to compute some of the potential energy surfaces relevant to this reaction. If curve crossings are involved, then we expect the statistical model we have used to treat the

process to be applicable.

Work is also being planned on the problem of dissociation of small polyatomic molecules by infrared lasers. It would seem that classical (or semiclassical) methods should be most useful to simulate this process since the molecular dynamics of highly excited vibrational states seems to be an integral part of the mechanism.

We also have some ideas on how to approach the inverse scattering problem for complex potentials. If these are successful this would be a great deal of help in analyzing experiments involving collisional ionization, such as Professor Lee's measurements of elastic scattering of metastable helium atoms by H_2 and by argon.

7. 1976 PUBLICATIONS AND REPORTS

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Papers at Meetings and Invited Lectures

1. Invited series of 4 lectures on "Semiclassical Scattering Theory", Hahn Meitner Institute for Nuclear Physics, Berlin, January 26-30, 1976.
2. Invited series of 3 lectures on "Semiclassical Scattering Theory", Niels Bohr Institute, Copenhagen, February 11-13, 1976.
3. Major invited paper, "Semiclassical Collision Theory", 2nd International Congress of Quantum Chemistry, New Orleans, April 19-24, 1976.
4. Invited series of 3 lectures on "Semiclassical Scattering Theory", University of Munich, March 16-21, 1976.
5. Guest Lecturer of the Nobel Institute of Physics, series of 3 lectures at the Quantum Chemistry Institute, Uppsala, Sweden, May 19-21, 1976.
6. Two invited papers, "Semiclassical Theory for Non-Separable Systems" and "Semiclassical Methods for Vibrational Energy Levels of Triatomic Molecules", Faraday Discussion on Potential Energy

Surfaces, University of Sussex, Brighton, September 8-10, 1976.

7. Invited paper, "Unified Statistical Model for 'Complex' and 'Direct' Reaction Mechanisms", at Energy Transfer Processes in Chemical Reactions (sponsored by the Bunsen Gesellschaft), Königstein, Germany, September 13-16, 1976.

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1. A. P. Hickman, A. D. Isaacson and W. H. Miller, Penning Ionization of H_2 by $He(2^3S)$: Quantum Mechanical Scattering Calculations within the Rigid-Rotor Approximation, J. Chem. Phys., LBL-5483, September 1976.
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f. Photoelectron Spectroscopy

David A. Shirley, Principal Investigator

Introduction. In 1976 the activities of this group were concentrated in two areas: (1) Photoemission studies of solids were focused on surface phenomena and on adsorbates, and angle-resolved photoemission was emphasized; (2) New work on gases was directed toward absorption, fluorescence, and direct lifetime measurements in rare-gas atoms and molecules. The research activities of the group are becoming increasingly involved with synchrotron radiation.

1. THE ORIENTATION OF CO ON Pt(111) AND Ni(111) SURFACES FROM ANGLE-RESOLVED PHOTOEMISSION

P. S. Wehner, G. Apai, J. Stöhr, R. S. Williams, and D. A. Shirley

The interaction of chemisorbed adsorbate molecules with catalytically active substrates has formed the focus of much recent research activity in surface physics. Because of the importance of the CO/Pt and CO/Ni systems in heterogeneous catalysis for synthesis of hydrocarbons, these systems have served as prototypes for surface studies. Until now, however, no firm evidence has been presented regarding the orientation of adsorbate CO molecules on crystalline nickel or platinum surfaces.

Davenport¹ presented SW X α calculations of photoelectron angular distributions from the molecular orbitals of oriented CO molecules and pointed out that chemisorbed CO should display similar angular distributions provided that the molecular wavefunctions are not strongly perturbed by the substrate. Our data for CO adsorbed on both Pt(111) and Ni(111) provide definitive evidence that the CO molecules "stand up" in both cases, with the carbon atoms bonded to the substrate and show that the t_{2g} orbitals of the Pt 5d band are strongly involved in the Pt-C chemisorption bond.

The experiments were carried out using the $h\nu = 40.8$ eV radiation emitted by a He II resonance lamp. Single crystals of Pt and Ni were cut along the (111) planes and cleaned in situ under ultrahigh vacuum conditions. In the angle-dependent studies both the unpolarized photon beam and the propagation direction of the analyzed electrons were in a horizontal plane, and the crystal could be rotated about a vertical axis in the plane of the (111) surface. Angle-resolved photoemission (ARP) was facilitated by masking all but an 11° arc of a cylindrical mirror analyzer, yielding an effective angular resolution of $(5 \pm 1)^\circ$ half angle. Figure 1 shows the variation of the clean valence-band spectra (solid line) and the corresponding spectra after adsorption of ~ 4 L CO (dotted line), plotted against θ , the angle of rotation from the crystal normal to the photoelectron $\vec{k}$ direction, for both crystals. The spectra shown in Fig. 1 were recorded with an experimental resolution of ~ 0.2 eV.

Fig. 1. Photoemission spectra of clean Ni(111) and Pt(111) (solid lines) and Ni(111) + 4L CO and Pt(111) + 4L CO (dotted lines) at $h\nu = 40.8$ eV as a function of the angle θ between the surface normal and the photoelectron propagation direction. θ is defined in Fig. 2a. (XBL 766-2963)

The CO molecular orbitals labeled A and B in Fig. 1 are manifest as two peaks falling at ~ 8.1 and ~ 10.8 eV binding energy below the Fermi level (E_F) in Ni and at ~ 9.2 and ~ 11.7 eV in Pt, respectively. The higher binding energy (E_B) peak (B) has been assigned to the 4σ orbital of CO, while the lower E_B peak (A) is attributed to a combination of the 1π and 5σ orbitals. In both cases the two peaks are of nearly equal intensity for $\vec{k}$ near the surface normal, with the B/A ratio decreasing as $\vec{k}$ is rotated toward the crystal surface. In Fig. 2c we have plotted the intensity ratio I_B/I_A of the two molecular orbitals A and B for the case of CO on Ni(111) and CO on Pt(111) as a function of the angle (θ) between the surface normal and photoelectron propagation direction. The details of the crystalline orientation with respect to the photon beam and the detector are shown in Figs. 2a and 2b. In Fig. 2d we have plotted the angular dependence

Fig. 2 (a) Experimental arrangement of the photon beam and detector with respect to the crystal normal. θ is defined positive for clockwise rotation, negative for anticlockwise rotation of the crystal normal with respect to the fixed photoelectron propagation direction into the analyzer. (b) Experimental orientation of the crystals in the (111) plane. (c) Intensity ratio I_B/I_A of the two molecular orbital peaks A and B in Fig. 1 as a function of θ . (d) Calculated intensity ratio $4\sigma/(1\pi+5\sigma)$, scaled to best fit experiment, for three orientations of the CO molecule with respect to the surface as a function of θ . (XBL 769-3919)

of the ratio $4\sigma/(1\pi+5\sigma)$ calculated from Davenport's angular distributions, for three orientations of the CO molecule with respect to the surface. The calculations have been scaled for the best fit to the experimental curves. We believe this is justified because Davenport's calculation does not predict the correct magnitude for the total cross section of the 1π and the 4σ orbitals at $h\nu \approx 41$ eV. For this reason we compare our results only to the angular dependence of the ratio and not the absolute magnitude.

In our calculation we take the unpolarized incident radiation to be composed of two orthogonal linearly polarized components one of which is in the plane containing the incoming photon beam and the detector and the other is perpendicular to this plane ($\vec{A} = \vec{A}_{\parallel} + \vec{A}_{\perp}$). The contributions from the two components to the differential photoemission cross section were calculated from an analytical expression.¹

Comparison of the experimental intensity ratio I_B/I_A for the adsorbate-substrate systems (Fig. 2c) with the scaled theoretical intensity ratio $4\sigma/(1\pi+5\sigma)$ for an oriented CO molecule (Fig. 2d) strongly favors the configuration where CO stands up, with the C bonded to the substrate. Note in particular that the configuration with O bonded to the substrate can be excluded because the $4\sigma/(1\pi+5\sigma)$ ratio vanishes for angles $\theta \geq 20^\circ$. We feel that the present results, besides determining the orientation of CO on Ni(111) and Pt(111), also prove in general that angle resolved ultraviolet photoemission can be used to determine bonding geometries. The different behavior of the ratio I_B/I_A

with θ for CO on Ni(111) and CO on Pt(111) may be due to a difference in the detailed nature of the adsorbate-substrate bonding for the two systems resulting in initial and/or final state effects which determine the photoemission angular distributions.² This point is currently under more thorough investigation.

The d-bands of Pt rise sharply to a peak very near E_F , then show a broad structure extending for about 7 eV. We have calculated the band structure of Pt using Smith's³ parametrization of the Hodges, Ehrenreich, and Lang⁴ tight-binding interpolation scheme. Figure 3 shows the calculated total valence band (VB) density of states and its decomposition into the t_{2g} and e_g components. The first VB peak near E_F is seen to arise in large measure from t_{2g} orbitals, which, because of high surface sensitivity of the photoemission spectra at $h\nu = 40.8$ eV, should mainly be located on surface Pt atoms.⁵ The dramatic decrease in the intensity of this peak on chemisorption of CO, which is evident in most of the Pt spectra in Fig. 1, indicates the involvement of surface t_{2g} orbitals in the chemisorption bond (s). A similar effect⁶ has also been observed at higher photon energies.

Fig. 3. Total valence band (VB) density of states and the t_{2g} and e_g projections for Pt 5d calculated in a tight binding interpolation scheme as discussed in the text. The density of states histograms were convoluted with a Gaussian of FWHM = 0.5 eV. (XBL 764-2737)

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2. PHOTOEMISSION FROM CO ON Pt(111) IN THE RANGE $40 \text{ eV} \leq \hbar\omega \leq 150 \text{ eV}$

G. Apai, P. S. Wehner, J. Stöhr, R. S. Williams, and D. A. Shirley

We report photoemission studies of CO on Pt(111) using 40 to 150 eV synchrotron radiation. This system was chosen because of its relevance to the Fischer-Tropsch synthesis in which platinum serves as a catalyst for the hydrogenation of carbon monoxide. Our main goal was to assess the feasibility and value of photoemission experiments on an adsorbate-substrate system using variable photon energies above 100 eV.

A specific purpose of this study was to learn how the photoemission spectrum is modulated by cross-section effects. Furthermore, it was intended to select an appropriate energy range for future angle-resolved studies. Accordingly two kinds of photoemission studies are reported below. First, we report measurements on the 5d VB of clean Pt in the energy range 40 to 200 eV. These studies were carried out at low resolution and are analyzed to yield the effective Pt 5d photoemission intensity as a function of photon energy. Secondly, the valence-band region of a clean Pt(111) crystal and that of Pt(111) with CO adsorbed have been investigated in the energy range $40 \text{ eV} \leq \hbar\omega \leq 150 \text{ eV}$.

Photoemission experiments were carried out at the 4° beam line of the Stanford Synchrotron Radiation Project (SSRP)¹ using ultra-soft x-ray radiation emitted by the circulating electrons in the storage ring SPEAR. A schematic diagram of the experimental geometry is shown in Fig. 1. The crystal orienta-

tion was adjusted for maximum photoemission intensity into the 360° acceptance cone of a double-pass cylindrical-mirror energy analyzer (CMA), operated in the retarding mode. The base pressure in the sample chamber was $\leq 1 \times 10^{-10}$ Torr.

In the experiments designed to study the variation of the Pt VB photoemission peak intensity with photon energy, spectra were recorded at a CMA pass energy of $E_p = 100 \text{ eV}$, corresponding to a resolution of 1.6 eV. The Pt 5d-band intensity was defined as the area under the photoelectron energy distribution extending from the Fermi energy to about 7 eV binding energy (BE), corrected for inelastic scattering. The area was normalized with respect to the incident photon flux and the collecting efficiency of the CMA.² The resulting energy dependence for the Pt 5d intensities at photon energies ranging from 40 to 200 eV is shown as the solid curve in Fig. 4.

The variation of the Pt VB peak intensity is of interest because it is closely related to the energy dependence of the Pt 5d ionization cross section. In fact, a direct proportionality between the VB intensity and its cross section would exist in the limit of weak final-state band structure effects.² Whether or not such effects alter the observed spectrum depends on the type of experiments performed. For example, in angle resolved photoemission from d-band metals dramatic changes in the shape of the spectra have been observed up to $\hbar\omega = 200 \text{ eV}$,³ while for polycrystalline d-band metals final-state band structure effects appear to be weak above 80 eV.^{2,4} In the present case yet another experimental situation is encountered because only the total energy-integrated intensity of the spectrum rather than its detailed shape is of interest. It is apparent that this type of measurement is far less sensitive to final-state band structure effects than is an energy-resolved spectrum. We believe that the modulation of the Pt 5d intensity due to final-state effects does not exceed $\pm 20\%$.

Our results for CO adsorbed on Pt reveal that there is a dramatic enhancement of CO spectral intensity relative to the Pt VB peak as a function of photon energy. Experimental results for clean Pt(111) and Pt(111) + 5 L CO are displayed in Fig. 2 as solid and dashed curves, respectively. The spectra were recorded with a CMA energy resolution of 0.8 eV. Common features of all spectra are the two peaks at $\sim 8.7 \text{ eV}$ (P_2) and $\sim 11.8 \text{ eV}$ (P_1) binding energy (BE) relative to the Fermi level. We attribute P_1 and P_2 to the 4σ and $(5\sigma + 1\pi)$ CO molecular orbitals respectively. Their BE's for the Pt(111) face agree with those obtained on polycrystalline Pt.⁵ The CO spectral intensity relative to the Pt VB, while poor up to $\hbar\omega = 70$ to 80 eV , is quite favorable at $\hbar\omega = 150 \text{ eV}$: in fact, better by a factor of three than at $\hbar\omega = 40 \text{ eV}$. The variation of ratio of the substrate and the adsorbate intensities with photon energy shown in Fig. 3 was derived in the following way. The experimental spectra (dashed curves in Fig. 2) were corrected for their inelastic backgrounds. The Pt 5d VB was defined over the range $E_F \leq BE \leq 7 \text{ eV}$ and its intensity was then compared to the area under the peaks P_1 (4σ) and P_2 ($5\sigma + 1\pi$).

We attribute this adsorbate intensity enhancement to the steep decrease in the Pt 5d intensity between 100 and 150 eV (escape depth probably varies

Fig. 1. Experimental arrangement for photoemission studies. Electrons are analyzed by a cylindrical mirror analyzer (CMA). (XBL 764-2732)

Fig. 2. Photoemission spectra of clean Pt(111) and Pt(111) + 5 L CO in the energy range $40 \text{ eV} \leq \hbar\omega \leq 150 \text{ eV}$. Experimental resolution was 0.8 eV.

(XBL 764-2733)

Fig. 3. Intensity of the CO peaks P_1 (4σ , 11.8 eV BE) and P_2 ($5\sigma+1\pi$, 8.7 eV BE) relative to the Pt 5d valence band intensity as a function of photon energy.

(XBL 763-2370)

Fig. 4. Plot of the theoretical CO ($5\sigma+1\pi$) cross section from Ref. 6 and the experimental Pt 5d VB intensity. The resultant ratio is plotted as a function of photon energy in the insert on a linear scale.

(XBL 764-2786)

by a factor of 2 or less, while the atomic cross section varies by more than an order of magnitude). For comparison we have plotted in Fig. 4 the theoretical differential photoionization cross section of the ($5\sigma+1\pi$) molecular orbitals of CO as a function of incident photon energy⁶ together with our experimental intensities for clean Pt. We realize the limitations of a plane wave (PW) final state calculation for CO for quantitative comparison with experimental cross sections. However, for lack of any more reliable theoretical or experimental results we have used the PW CO cross sections shown in Fig. 4 to predict the ratio of the P_2 ($5\sigma+1\pi$) CO peak intensity relative to the Pt 5d VB intensity. The results, shown inserted on a linear scale in Fig. 4, are in good qualitative agreement with the experimental results in Fig. 3.

The above model can also account for the relative cross sections of CO on Ni and Pd. Gustafsson, et al.⁷ found that the surface adsorbate signal falls off much more rapidly for CO on Ni than for CO on Pd. Ni is a 3d VB metal and as such should have a gradual monotonically decreasing intensity with increasing photon energy much like Cu.⁴ For this case the CO spectral intensity falls off more rapidly than the Ni VB intensity, giving a monotonic decrease of the surface adsorbate signal, relative to that of the substrate. On the other hand Pd is a 4d VB metal with a radial node in the 4d wavefunction and as such should exhibit a Cooper minimum similar to the 4d VB of Ag.² The Ag intensity remains nearly constant for $40 \text{ eV} \leq \hbar\omega \leq 80 \text{ eV}$, then falls precipitously by over an order of magnitude to a minimum at $\hbar\omega \sim 140 \text{ eV}$. The Pd 4d wavefunction should exhibit a similar pattern. We credit this Cooper's minimum in the Pd VB intensity with the increase in relative adsorbate emission

for Pd at $\hbar\omega \approx 80$ eV. The restriction of photon energy to $\hbar\omega \leq 100$ eV precludes Gustafsson et al. from observing the full extent of MO enhancement. Our studies with a monolayer of CO adsorbed on Pt show that future adsorbate studies benefit from synchrotron studies at high photon energies because of the selectivity for reducing substrate background intensity.

Finally, we would like to comment on another general observation. When CO adsorbs on the (111) face of Pt, the peak nearest the Fermi level always decreases in intensity relative to the other peaks in the Pt valence band (see Fig. 2). This seems to indicate that the states nearest the Fermi level are donating electrons to the CO molecule as it adsorbs. The observation that the Pt denotes electrons to the CO molecule and not vice versa is supported by work-function measurements.⁸

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3. PHOTOEMISSION STUDIES OF ELECTRON STATES AT CLEAN SURFACES USING SYNCHROTRON RADIATION

J. Stöhr, P. S. Wehner, R. S. Williams, G. Apai, and D. A. Shirley

Photoemission spectra of valence bands exhibit both bulk and surface features. As is shown in Fig. 1 the study of surface-derived effects is greatly aided by the availability of synchrotron radiation. Since the photoelectron mean free path in most materials is shortest at a kinetic energy around 100 eV, the photocurrent in this energy range arises largely from the surface layer of the material. A special advantage of using synchrotron radiation rather than laboratory photon sources (see Fig. 1) is that one can tune into the surface-sensitive energy range and thus enhance surface over bulk effects. In the following we shall discuss two examples of such studies carried out at the Stanford Synchrotron Radiation Project (SSRP) on the storage ring SPEAR.

Fig. 1. Photoelectron mean free path (attenuation length) as a function of electron energy. The shaded area represents the scatter encountered for various solid materials. Available laboratory photon sources are indicated as vertical lines. The Stanford Synchrotron Radiation Center currently provides monochromatic radiation in the range $5 \text{ eV} \leq h\nu \leq 650 \text{ eV}$ and $h\nu \geq 4000 \text{ eV}$. (XBL 755-3056)

The first example demonstrates that the bulk band structure is modified at the surface. This result is intuitively expected and has been predicted theoretically for several years. The most interesting result of such calculations is the prediction of a narrowing of the d-band density of states near the surface.¹ In a simple physical picture such a behavior is expected because the reason for broadening atomic levels into solid-state bands is partly removed at the surface. This effect is demonstrated experimentally in Fig. 2 by using angle resolved photoemission from the (001) and (111) faces of a Cu single crystal. Electrons were taken off along the [001] direction either normal to a (001) face ($\alpha = 90^\circ$) or at a take-off angle $\alpha \approx 35^\circ$ with respect to a (111) face. Similarly, spectra were obtained for propagation along the [111] direction of a (111) crystal ($\alpha = 90^\circ$) and a (001) crystal ($\alpha = 35^\circ$). As seen from Fig. 2 there are distinct differences between spectra corresponding to electron propagation along the same crystalline direction at high and low take-off angles. In both cases the spectra obtained at low take-off angles ($\alpha = 35^\circ$) exhibit a narrowing in d-bandwidth and increase in height at their center of gravity. As seen from Fig. 3, the above change in angle corresponds to a decrease in effective sampling depth inside the crystal by a factor of approximately 2. In the low take-off angle case the surface-derived contribution to the spectrum is considerably enhanced. The fact that the escape depth is already short at $h\nu = 90$ eV (see Fig. 1) makes us believe that we are largely sampling the outermost layer of the crystal in the low take-off angle case.

Fig. 2. a) Comparison of photoemission spectra of Cu taken from electrons propagating along an [001] direction normal to an (001) crystal face ($\alpha = 90^\circ$) and at a take-off angle of $\alpha = 35^\circ$ from a (111) crystal face. b) Spectra taken along a Cu [111] direction normal to a (111) crystal face ($\alpha = 90^\circ$) and at a take-off angle of $\alpha = 35^\circ$ from an (001) face. (XBL 764-2764A)

Fig. 3. The effective sampling depth inside the solid (shaded area) is decreased by using a lower take-off angle from the surface. Here we have assumed that the attenuation length L of the electron inside the solid is isotropic. (XBL 7611-9732)

4. ANGLE AND ENERGY DEPENDENT PHOTOEMISSION STUDIES OF PLASMON LOSS STRUCTURE IN Al AND In

R. S. Williams, S. P. Kowalczyk,* P. S. Wehner, G. Apai, J. Stöhr, and D. A. Shirley

The surface sensitivity of photoelectron spectroscopy is due to the relatively short inelastic mean free path λ for electrons traversing a solid with kinetic energy less than 1000 eV. The low cross sections for photoemission allow incident soft x-ray or ultraviolet radiation to penetrate at least 1000 Å into the bulk of a solid sample. However, the unbound electrons created in the sample

by absorption of photons have high cross sections for elastic and inelastic scattering¹ from the densely packed atoms of the solid. The elastic collisions preserve the magnitude of the photoelectron momentum, but change the direction of travel. Since as many electrons should be scattered toward the sample surface (and the electron detection system) as away from it, elastic scattering events need only be considered in detailed analysis of angle resolved photoemission studies along particular directions in well ordered systems. Inelastic collisions are characterized by changes (of any magnitude) in the photoelectron kinetic energy accompanied by only slight changes in the direction of travel. Thus a photoelectron which experiences one or more inelastic collisions will be removed energetically from the spectral feature of its origin and contribute instead to the "background" or "inelastic tail" which comprises most of a photoemission spectrum. Typically only photoelectrons originating in the uppermost 25 Å or less² of a solid sample reach the detector without suffering an inelastic collision.

Inelastic collisions involve mainly excitations of valence or core electrons. Valence electron excitations are conceptually divided into two categories.³ The short wavelength (or quasiparticle) excitation involves the simultaneous creation of an electron in the conduction band and a hole in the valence band. This quasiparticle excitation takes up a range of energies, contributing slight peak asymmetries to higher binding energies⁴ and relatively flat backgrounds to photoemission spectra. The long wavelength (or collective) excitation for nearly free electron-like metals adds one or more quanta to the surface or bulk plasma structure. Plasmon losses contribute discrete structure to photoemission spectra which are separated from main peaks by multiples of $\hbar$ times the bulk and surface plasmon frequencies (ω_b and ω_s).⁵ The quasiparticle and plasmon creation probabilities have the same order of magnitude, and both are roughly an order of magnitude greater than the core electron excitation probability.⁶ Thus the valence band structure of a material determines the inelastic mean free path λ_{ee} for photoelectrons, and this in turn can be studied through the electron loss structure in photoelectron spectra.

We have carried out the first angle and energy dependent photoemission studies of plasmon loss structure for Al and In and compared our results to several theoretical studies.^{2,5,6} Our angle resolved studies of Al plasmon losses were carried out using a monochromatized Al K α line source with photon energy 1486.6 eV. The photoelectron angular acceptance was a cone with a 4° divergence from the symmetry axis. Figure 1 shows the Al 2s peak and the first surface and bulk plasmon loss satellites for three different electron take-off angles. The spectra show that for lower take-off angles the surface plasmon intensity increases with respect to the main peak, whereas the bulk plasmon intensity remains fairly constant. This can be understood from the simple picture that the lower the take-off angle, the longer the effective distance traveled through the sample for electrons which finally reach the detector. Thus lowering the electron take-off angle enhances the surface sensitivity of a photoemission experiment. Figure 2 compares the angular dependence of the bulk to surface plasmon ratio as a func-

Fig. 1. The Al 2s spectral region as a function of take-off angle obtained using Al K α x-rays. (XBL 769-4044)

tion take-off angle for this study and for data taken from theoretical calculations by Šunjić and Šokcević.³ The theoretical curve was drawn assuming a total electron mean free path λ of 18 Å, which has been measured elsewhere by overlay techniques.⁷ The agreement of our data with the theoretical results show that experimental values for λ can be determined for other photoelectron energies and other materials through comparisons such as that in Fig. 2.

Our energy dependent studies utilized synchrotron radiation from the 4th station of Beam Line I at the Stanford Synchrotron Radiation Project. The electron energy analyzer operated in an angle integrated mode which accepted electrons from normal to about 7° take-off angle. Figure 3 shows some spectra obtained for Al 2p and associated plasmon losses at several photon energies. Figure 4 shows the plasmon intensities as a function of photon (and kinetic) energies. Although no calculations have been performed to relate plasmon intensities to λ in this energy regime, we can predict qualitatively the appearance of the λ vs. photoelectron kinetic energy relationship. A minimum in λ should occur at the same energy as the minimum in the bulk to surface plasmon ratio. From Fig. 4 this minimum is estimated to occur at 70 eV kinetic energy whereas rough calculations of λ vs. energy in Al have indicated minima occurring at 15 and 50 eV.^{2,6} Figure 5 shows spectra obtained for In 4d plus plasmon losses for several photon energies. The most interesting feature to note in these spectra,

Fig. 2. The variation of surface to bulk plasmon ratios (I_B/I_S) as a function of electron take-off angle ϕ is shown. The solid line is the theoretically predicted ratio taken from Ref. 3. The dashed continuation of the solid curve is proportional to $\sin \phi$. (XBL 7611-4452)

Fig. 3. The Al 2p spectral region taken at various photon energies in the ultra-soft x-ray regime is shown. The spectrum taken at a photon energy of 170 eV has a peak due to the Al L_IL_{II}, L_{III}M Auger transitions, which interfered with the plasmon loss peaks and Al 2p peak for incident photon energies between 130 eV and 170 eV. (XBL-769-4042)

Fig. 4. The upper portion of the figure shows the photoelectron energy dependence of the Al 2p bulk to surface plasmon ratio (solid circles from this work, solid squares from Ref. 8). The lower portion displays the plasmon to main peak intensity ratios for the first surface (crosses from this work, solid squares from Ref. 8) and bulk (solid circles from this work, diamonds from Ref. 8) loss features.

(XBL 7611-4455)

Fig. 5. The In 4d spectral region obtained at various photon energies in the ultra-soft x-ray regime.

(XBL 769-4043)

Fig. 6. The energy variation of plasmon to In 4d no loss peak intensity ratios is shown for the first surface (crosses) and bulk (solid circles) loss structures.

(XBL 7611-4456)

as emphasized in Fig. 6, is the striking increase in intensity of the surface plasmon with respect to the main peak and the bulk plasmon in the spectrum taken at a photon energy of 160 eV. This sudden dip in λ is not yet understood.

We have thus seen that the study of electron loss structure in PES can provide information on the electron mean-free-path in solids. We can use this information by choosing electron take-off angles and photon energies to sample either bulk or surface properties of solids selectively. Further, the study of electron loss properties yields valuable information on the valence band structure of materials and the many-body nature of photoemission.

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5. d-ORBITAL DIRECTED PHOTOEMISSION FROM COPPER

G. Apai, J. Stöhr, P. S. Wehner, R. S. Williams, S. P. Kowalczyk,* and D. A. Shirley

Angle-resolved x-ray photoemission has recently been shown^{1,2} to yield strong directional variations in the valence band spectra with respect to the crystalline axes of single-crystal samples. Unfortunately, the interpretation of such spectra is in general a nontrivial problem since no final-state band structure calculations exist at such high energies, thus precluding detailed calculations. However, an approximate model based on the symmetry properties of the initial state wavefunctions has recently been put forth by this group² which accounts for the general features of the spectra. An analytical expression for this "matrix-element" model is presented here for photoemission from tight-binding d-bands into plane-wave final states. This expression allows one to calculate the angle-resolved photoemission (ARP) spectra for any photoemission direction with respect to the crystalline axes by means of a linear combination of atomic orbitals carried out in 1/48 of the Brillouin zone (BZ). The results of such calculations for photoemission along the [001] and [111] directions for Cu are presented and shown to be in excellent agreement with experimental results.

The present model was first discussed by McFeely, et al.² in connection with angle-resolved photoelectron energy distributions (PED's) from Ag and Au valence bands. In this paper the authors pointed out that a realistic description of the final states (i.e., Bloch sums rather than free-electron states) in conjunction with the finite acceptance angle of the analyzer, leads to sampling of all states in the first BZ. This point is illustrated in Fig. 1b, for

Fig. 1. (a) (010) projection of the three-dimensional Brillouin zone (BZ) of a fcc lattice with lattice constant a . The $\vec{k}$ axes are those of the infinite three-dimensional crystal. (b) Photoemission at $h\nu = 1486.6$ eV along the [001] direction assuming an angular resolution of $\pm 4^\circ$ and Bloch-like final states. Because of mixing of the free electron final states by the crystalline potential initial states almost throughout the entire first BZ (dashed area) may contribute to photoemission to final Bloch states containing $\vec{G} = [0,0,12]$ components. The whole first BZ may contribute if the photon wave-vector is taken into account as discussed in the text. (XBL 7611-9936)

photoemission in the [001] direction with an angular divergence of $\pm 4^\circ$ and $\vec{k}_{ph} = 0$ as an example. Because in a realistic band structure the final state wavevector and energy are no longer related by the simple free electron dispersion relation $E_f(\vec{k}) = \hbar^2 |\vec{q}|^2 / 2m$ the magnitude of $\vec{q}$ inside the crystal is no longer fixed.² At $h\nu = 1486.6$ eV a great number of final Bloch states contain the reciprocal lattice vector $\vec{G} = [0,0,12]$ and all such possible final states, which can enter the analyzer, are indicated as the shaded area in Fig. 1b. When reflected back into the first BZ by $\vec{G} = [0,0,-12]$ the shaded area indicates all initial states which may contribute to photoemission into the analyzer. Here it is important to state that even the small parts of the first BZ which cannot undergo transitions to final Bloch states containing $\vec{G} = [0,0,12]$ components may contribute if $\vec{G} = [0,0,14]$ components are considered or if the effect of the photon-wavevector ($\vec{k}_{ph}$) is taken into account. Thus from a standpoint of momentum conservation initial states within the whole first BZ may give rise to photoemission into a $\pm 4^\circ$ acceptance cone along the [001] direction, or in general along any given direction. However, in order for transitions to occur from a given initial state both momentum ($\vec{q} = \vec{k}_{ph} + \vec{k} + \vec{G}$) and energy ($E_f(\vec{k}) = E_i(\vec{k}) + \hbar\omega$) need to be conserved in the excitation process. In the XPS regime of photoemission the energy conservation selection rule is relatively easily fulfilled at points throughout the first BZ because of the large number of final states present and the mixing of these states by the crystal potential. This point is discussed in more detail by McFeely, et al.²

Using the above assumption, that the whole BZ contributes to photoemission, it can easily be shown that the angle dependent PED's are given by just the initial density of states where the various bands at each $\vec{k}$ -point are weighted by an angle-dependent transition matrix element. As was shown in Ref. 2, this transition matrix element may conveniently be calculated by writing the initial state wavefunction in the tight-binding form² and assuming a plane-wave final state. Neglecting the s-part of the initial state wavefunction, which only contributes a small and isotropic matrix element, one obtains the angle-dependent matrix element²

$$\sigma(\vec{k}, j, \vec{q}) \sim \left| \sum_{\mu=1}^5 \beta_{\mu}^j(\vec{k}) d_{\mu}(\theta_q, \phi_q) \right|^2 \quad (1)$$

and the intensity distribution may be discussed in terms of the Fourier transformed d-orbitals $d_{\mu}(\theta_q, \phi_q)$ listed in Table 1. The coefficients $\beta_{\mu}^j(\vec{k})$ are obtained from a band-structure calculation. Equation (1) may be further simplified by grouping the matrix elements of all equivalent points in the first BZ. In this way it is seen that the various cross-terms which occur in Eq. (1) cancel and one obtains the following analytical expression for the matrix element

$$\sigma(\vec{k}, j, \vec{q}) \sim 2 \left(|\beta_1^j|^2 + |\beta_2^j|^2 + |\beta_3^j|^2 \right) (d_1^2 + d_2^2 + d_3^2) + 3 \left(|\beta_4^j|^2 + |\beta_5^j|^2 \right) (d_4^2 + d_5^2). \quad (2)$$

Table 1. Angular d-Orbitals.

Label		Function
d_1	d_{xy}	$(15/4\pi)^{1/2} \sin^2\theta \sin\phi \cos\phi$
d_2	d_{yz}	$(15/4\pi)^{1/2} \sin\theta \cos\theta \sin\phi$
d_3	d_{xz}	$(15/4\pi)^{1/2} \sin\theta \cos\theta \cos\phi$
d_4	$d_{x^2-y^2}$	$\frac{1}{2}(15/4\pi)^{1/2} \sin^2\theta \cos 2\phi$
d_5	$d_{3z^2-r^2}$	$\frac{1}{2\sqrt{3}} (15/4\pi)^{1/2} (3\cos^2\theta - 1)$

Because in deriving Eq. (2) we have transformed the wavefunction of all equivalent points in the first BZ into one irreducible wedge of the BZ one may use Eq. (2) as weighting factors for a density of states calculation in the $1/48$ BZ. The angle-resolved photoemission spectrum in the XPS limit is then given by

$$N(E, \vec{q}) \sim \int_{1/48 \text{ BZ}} d^3k \sum_j \sigma(\vec{k}, j, \vec{q}) \delta(E - E_j(\vec{k})). \quad (3)$$

According to Eq. (2) photoemission along the [001] direction ($\theta_q, \phi_q = 0^\circ$ and hence $d_1 = d_2 = d_3 = 0$) and along the [111] direction ($\theta_q = 57.7^\circ$, $\phi_q = 45^\circ$ and hence $d_4 = d_5 = 0$) represent the two extreme cases corresponding to the e_g and t_{2g} projections of the density of states.

In Fig. 2 we show the results of a theoretical calculation employing Eq. (3) for photoemission along the [001] and [111] direction from the valence bands of Cu together with the experimentally determined PED's. The experimental spectra obtained with monochromatized AlK α radiation are shown in Fig. 2a. The first spectrum was obtained earlier from a polycrystalline Cu sample. The other two spectra were recorded using two single crystal samples. They correspond to electron propagation along the [111] and [001] directions, respectively. The detailed shapes of the Cu[111] and Cu[001] PED's are compared in Fig. 2b. It is apparent that a distinct change in spectral shape exists between the two angle resolved PED's. In Fig. 2c we show the results of the calculation, i.e., the e_g and t_{2g} projections of the density of states. Comparison of Figs. 2b and 2c reveals good agreement between the experimental shapes of the PED's and the calculated ones. The main characteristic differences between the experimental spectra taken along the two symmetry directions are predicted well by the calculation. We note that plane-wave final state cross section calculations should be more reliable for Cu than for the previously investigated noble metals Ag and Au.² This is inferred by the small electron scattering phase shifts for Cu as opposed to the larger values for Ag and Au. Also, the spin-orbit coupling which reduces the $e_g - t_{2g}$ anisotropy by mixing the wavefunctions is small for Cu.

Fig. 2. (a) Experimental photoemission spectra from valence bands of Cu using AlK α radiation. The first spectrum was obtained with a polycrystalline (evaporated) Cu sample. The second spectrum was measured along the [111] direction, and the third spectrum along the [001] direction of a single crystal. (b) Comparison of the Cu[111] and Cu[001] spectra of Fig. 1a. (c) Calculated t_{2g} and e_g projections of the total Cu 3d density of states using a tight binding interpolation scheme as discussed in the text. The density of states histograms were convoluted with a Gaussian of FWHM = 0.8 eV. (XBL 765-2894)

More evidence for the importance of matrix element effects in x-ray photoemission from d-bands was recently presented by Williams, et al.³ These authors found good agreement between the angular variation of valence band peak intensities of MoS₂ and that predicted by a tight-binding d initial and plane-wave final state matrix element. We feel that the present results in conjunction with the results obtained earlier² for Ag and Au indicate that the model presented above to explain the angular dependence of photoemission from d-bands may in general provide a useful approximation in the x-ray range of photoemission.

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6. INTERPRETATION OF ANGLE-RESOLVED X-RAY PHOTO-EMISSION FROM VALENCE BANDS

P. S. Wehner, J. Stöhr, G. Apai, F. R. McFeely,*
and D. A. Shirley

Angle-resolved x-ray photoemission has recently been shown¹⁻³ to yield strong directional variations in valence band spectra with respect to the crystal-line axes of single-crystal samples. A definitive explanation of this effect would be highly desirable because of its diagnostic potential. Computational difficulties preclude a rigorous solution of the problem (in contrast to angle-resolved ultraviolet photoemission) but two approximate models have recently been put forth to account for the general features of the spectra.^{1,2} Both models are physically reasonable, and both involve substantial mathematical approximations. Neither is therefore to be preferred *a priori*: any preference must be based on the relative abilities of the two models to predict experimental spectra. We shall first state the assumptions inherent in each model, then compare the spectra predicted by each model to experiment.

Both models begin with the same expression for the photoemission energy distributions (PED's) which has been successfully used at UPS energies⁴

$$N(E, h\nu) \sim \int_{\text{BZ}} d^3k \sum_{i,f} |t_{fi}(\vec{k})|^2 \delta(\vec{k}_f - \vec{k} - \vec{k}_{h\nu} - \vec{G}) \times \delta(E_f(\vec{k}) - E_i(\vec{k}) - h\nu) \delta(E(\vec{k}) - E_i(\vec{k})). \quad (1)$$

Here $t_{fi}(\vec{k})$ is a transition matrix element between an initial state of wavevector $\vec{k}$ and energy $E_i(\vec{k})$ and a final state of wavevector $\vec{k}_f$ and energy $E_f(\vec{k})$. The δ -functions represent the requirements of momentum and energy conservation in the excitation process; $\vec{k}_{h\nu}$ is the photon wavevector and $\vec{G}$ is a reciprocal lattice vector. The two models differ in the relative importance they attribute to the various terms in equation (1).

The model proposed by Baird et al.¹ is based on the following three assumptions:^{1,5}

- (1) The final state band structure is free-electron-like, i.e., the various bands are only weakly mixed by the crystal potential.
- (2) The states within the first BZ which contribute to the photoemission spectrum are determined by momentum and energy conservation using a free electron final state band structure.
- (3) All states determined by the momentum and energy conservation selection rules contribute equally to photoemission, i.e., all transition matrix elements are the same.

With these assumptions equation (1) reduces to

$$N(E, h\nu) \sim \int_{\text{BZ}} d^3k \sum_i \delta(\vec{k}_f - \vec{k} - \vec{k}_{h\nu} - \vec{G}) \times$$

$$\delta(E_f(\vec{k}) - E_i(\vec{k}) - h\nu) \delta(E(\vec{k}) - E_i(\vec{k})), \quad (2)$$

which is just the density of (initial) states evaluated over those $\vec{k}$ values and states in the first Brillouin zone (BZ) which satisfies the momentum and energy conservation selection rules. In this model angular variations in the photoemission spectrum arise because different parts of the first BZ are sampled for different photoemission directions.

The second model, proposed by McFeely, et al.,² takes a completely different approach and assumes:^{2,6}

- (1) The final state band structure is Bloch-like, i.e., the various bands are strongly mixed by the crystal potential.
- (2) States throughout the first BZ contribute to photoemission, i.e., both momentum and energy conservation selection rules are satisfied for states distributed throughout the zone.
- (3) The transition matrix elements can be calculated using plane wave final state wavefunctions.

With these assumptions equation (1) reduces to

$$N(E, h\nu) \sim \int_{\text{BZ}} d^3k \sum_i |t_{fi}(\vec{k})|^2 \delta(E(\vec{k}) - E_i(\vec{k})), \quad (3)$$

which is the total density of (initial) states with the bands of each $\vec{k}$ point in the first BZ weighted by the square of the transition matrix element $|t_{fi}|^2$. This matrix element is easily evaluated using a tight-binding Bloch function for the initial state and a plane-wave function for the final state. It is found that the matrix element for a general photoemission direction is a linear combination of the t_{2g} and e_g projections of the initial state tight-binding Bloch functions. Thus, this model establishes a direct correspondence between the symmetry properties of the initial state wavefunction and the photoemission angular distribution.

Experimental and theoretical results for Au are compared in Fig. 1. Experimental spectra, taken from Ref. 1, are shown in the central column of the figure. The three spectra shown in Fig. 1b represent the basic spectral changes observed in angle resolved photoemission from Au (cf. Fig. 1 of Ref. 1).

Theoretical model calculations for Au are shown in Fig. 1a for the direct transition model proposed by Baird, et al.¹ and in Fig. 1c for the matrix element model proposed by McFeely, et al.² Both calculations were carried out using Smith's parametrization of the Hodges, Ehrenreich, and Lang (HEL) tight binding interpolation scheme to obtain the initial state band structure. The calculated spectra were convoluted with a 0.8 eV FWHM Gaussian.

Fig. 1. Comparison of experimental and calculated angle-resolved x-ray photoemission spectra of Au valence bands. The respective photoemission directions are indicated by the corresponding crystal-line directions $[hkl]$ as in Ref. 1. (a) Theoretical model calculations for the direct transition model as discussed in the text. (b) Experimental spectra taken from Ref. 1. (c) Theoretical model calculations for the matrix element model as discussed in the text. (XBL 7611-4442)

Comparison of the experimental spectra in Fig. 1b with the two theoretical results reveals better agreement with the matrix element model calculation (Fig. 1c). All of the main directional variations observed experimentally are reproduced by this model: for example, the much lower intensity and height of the higher binding-energy (BE) peak along [001], the essentially square-topped shape of the lower BE peak along [101], and the asymmetric peak shape along [111]. In fact with a little additional broadening the spectra in Fig. 1c would reproduce experiment almost quantitatively. By contrast, the direct-transition model predictions (Fig. 1a) fail in all three instances to show even qualitative agreement with experiment. Furthermore, they fail in other important respects. For example, too much structural variation is predicted. Thus the valley between the two main peaks is much too large for [001], while a spurious valley around 3 eV BE is predicted for [111]. Another serious discrepancy is the d-bandwidth (FWHM) predictions, which is largest for the [001] direction, in contrast to experiment and to the matrix-element model, which show the bandwidth to be narrowest in this direction. The error of the direct-transition model in this case is almost 1 eV. Inclusion of matrix-element effects in the direct-transition calculations only lessens the agreement, presumably because too little of the first BZ is sampled in the direct-transition model. We conclude that for gold the matrix-element model agrees better with experiment than the direct-transition model.

A similar comparison of experimental spectra and those predicted by the two models is shown in

Fig. 2. Comparison of experimental and calculated angle-resolved x-ray photoemission spectra of Cu valence bands. The respective photoemission directions are given in the central column in terms of polar (θ) and azimuthal (ϕ) angles with respect to the cubic crystalline axes. The upper two spectra correspond to $\phi=0$, the lower three correspond to $\phi=45^\circ$. (a) Theoretical model calculation for the modified direct transition model (Ref. 6). (b) Experimental spectra taken from Ref. 6. (c) Theoretical model calculation for the matrix-element model as discussed in the text. (XBL 7611-4437A)

Fig. 2 for the case of angle resolved photoemission from Cu. The experimental spectra in Fig. 2b and the direct-transition model calculations in Fig. 2a are taken from Ref. 5. Spectra calculated with the matrix-element model are shown in Fig. 2c. Both calculations employed Burdick's band structure of Cu to describe the initial state and in each case the calculated spectra were convoluted with a 0.8 eV FWHM Gaussian. As for the case of Au, the predicted spectral variations are too pronounced in the direct-transition calculation, and they do not follow the experimental variations. Thus, for example, from the second to the third spectra from the top of Fig. 2a, the direct-transition model predicts the d-band width (FWHM) to increase from 1.75 eV to 3.05 eV, while it in fact decreases from 2.9 eV to 2.75 eV. The matrix-element model predicts a decrease from 2.85 to 2.75 eV. In four of the five directions shown in Fig. 1, the matrix-element model shows excellent agreement with theory. In the [001]-direction spectrum the agreement is not as good. The direct-transition model prediction for this take-off direction is similar to that of the matrix-element model. It should be noted that the experimental resolution is quite low for this take-off direction, corresponding to ~ 1.4 eV FWHM of the Au 4f_{7/2} line.⁶ It is clear from Fig. 2 that con-

volution of the theoretical spectrum with a Gaussian of FWHM > 0.8 eV would considerably improve the agreement with experiment.

In summary, the present results indicate that angle resolved x-ray photoemission spectra from Au to Cu single crystals are well described by a model which relates the angular anisotropies in the photoemission intensity to an angle dependent transition matrix element. Such a model is found to predict the experimental PED's considerably better than the model previously proposed by Baird, et al.¹ The present results in conjunction with the results obtained by Williams, et al.³ on MoS₂ and GaSe appear to indicate that the matrix-element model discussed above may in general provide a useful approximation for the interpretation of angle resolved photoemission spectra in the x-ray range of photoemission.

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7. ATOMIC CROSS-SECTION EFFECTS IN SOFT X-RAY PHOTOEMISSION FROM Ag, Au, AND Pt VALENCE BANDS

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Photoemission spectra which are obtained by exciting valence electrons in solids depend mainly on three quantities: the initial state (valence band) band structure, the photoexcitation matrix element, and the final state (conduction band) band structure. The latter two define the photoemission cross section. The present study is concerned with the energy dependence of the valence-band (VB) cross sections of Ag (4d), Au (5d) and Pt (5d) in the range $32 \text{ eV} \leq h\nu \leq 250 \text{ eV}$. Studies of the present kind are of interest because it is known from atomic calculations that so-called "Cooper minima"¹ exist in the cross-section for initial state wavefunctions which exhibit a radial node. In such cases the cross section may vary strongly over a small energy range. One objective of the present paper is to investigate whether such effects can be observed in photoemission from 4d (one radial node) and 5d (two radial nodes) initial states.

Experiments were performed using synchrotron radiation from the storage ring SPEAR at SLAC.² The

incident monochromatic³ light was focused onto the samples which were positioned in the focal point of a double-pass cylindrical mirror analyzer (CMA) (see Fig. 1). The polycrystalline Ag samples were prepared by *in situ* evaporation from a tungsten filament onto a stainless-steel substrate. The Au sample was a polycrystalline foil which was cleaned by Ar⁺ bombardment and subsequently annealed by heating with an electron gun. Pt spectra were recorded using a single crystal with a (111) surface orientation. The crystal was cleaned by heating it to $\sim 950^\circ\text{C}$ in 5×10^{-6} Torr oxygen and then flashing it to $\geq 1000^\circ$ to remove oxygen. The base pressure in the sample chamber was $\sim 1 \times 10^{-9}$ for the experiment on Ag and $\leq 1 \times 10^{-10}$ Torr for Au and Pt. Spectra of the valence bands were recorded with a CMA pass energy $E_p = 100$ eV, corresponding to a resolution of 1.6 eV.

Fig. 1. Experimental arrangement for photoemission studies. Electrons are analyzed by a cylindrical mirror analyzer (CMA). (XBL 764-2732)

The experimental spectra of the VB region obtained this way were corrected for their inelastic background and the area under the respective d-valence band peaks was determined. For Ag and Au the s-band intensity in the d-band region was estimated by extrapolating the s-band intensity near the Fermi level to higher binding energy and subtracted from the total intensity. The area obtained this way for the d-band was normalized with respect to the average photon flux incident on the sample. The photon flux depends on both the electron-beam current of SPEAR at the time of measurement and the transmission of the mirror plus monochromator assembly at a given photon energy. The beam current and its decay during data collection (typical time ~ 30 minutes per spectrum) was supplied on line by SPEAR. The transmission of the mirror plus monochromator as a function of photon energy had previously been measured with a sodium salicylate scintillation counter.⁴ Finally, the data were corrected for the collecting efficiency of the CMA.⁵ Due to the action of the accelerating/retarding field the collecting efficiency is a function of both the pass energy (E_p) of the CMA and the kinetic energy (E_k) of the electrons emitted from the sample. The

transmitted current in general is theoretically given by $I \sim E_p/E_k$.⁵ Thus the observed 4d intensity at a given photon energy $\hbar\omega$ was corrected by a factor E_k/E_p where in our case $E_p = 100$ eV and $E_k = \hbar\omega - \phi$, where ϕ is the sum of the valence band binding energy and the work function.

Results for Ag are shown in Fig. 2. The strongest change in the VB intensity is observed for 100

Fig. 2. Relative intensity of the Ag 4d peak as a function of photon energy. The data were collected during three different beam periods (Run 1,2,3). The dashed curve neglects correction of the 4d intensity for the collecting efficiency of the CMA. (XBL 763-2373)

eV $\leq \hbar\omega \leq 140$ eV. Here the 4d intensity decreases by more than an order of magnitude and exhibits a pronounced minimum at $\hbar\omega = 140$ eV. In Fig. 3 we com-

Fig. 3. Relative intensity of the 4d valence band of Ag (compare Fig. 2) and the 5d valence band of Au as a function of photon energy. The Ag and Au valence band intensities were normalized with respect to each other at $\hbar\omega = 40$ eV. (XBL 764-2763)

pare the results obtained for Ag (4d) and Au (5d). The Ag and Au VB intensities were normalized with respect to each other at $\hbar\omega = 40$ eV. In contrast to Ag no pronounced minimum is observed for the Au 5d intensity. This is confirmed by measurements of the Pt 5d intensity shown in Fig. 4. The qualitative

Fig. 4. Relative intensity of the Pt 5d VB as a function of photon energy. (XBL 763-2371)

photon energy dependence of the 5d VB's of Au and Pt is very similar. In both cases the changes are weak in the region $40 \text{ eV} \leq \hbar\omega \leq 70 \text{ eV}$ and $\hbar\omega \geq 150 \text{ eV}$, while the intensity decreases strongly in the region $70 \text{ eV} \leq \hbar\omega \leq 150 \text{ eV}$. In this range the Au and Pt VB intensities decrease by factors of ~ 20 and ~ 45 , respectively.

The variation of the VB peak intensities is closely related to the energy dependence of the respective ionization cross sections.⁶ In fact, a direct proportionality between the VB intensity and its cross section would exist in the limit of weak final-state band structure effects.⁶ Whether or not such effects affect the observed spectrum depends on the type of experiments performed. For example, in angle-resolved photoemission from d-band metals dramatic changes in the shape of the spectra have been observed up to $\hbar\omega = 200$ eV,⁷ while for polycrystalline d-band metals final-state band structure effects appear to be weak above about 80 eV.^{6,8} In the present case yet another experimental situation is encountered because only the total energy-integrated intensity of the spectrum rather than its detailed shape is of interest. It is apparent that this type of measurement is far less sensitive to final-state band structure effects than is an energy-resolved spectrum. We believe that the modulation of the measured intensities due to final-state effects does not exceed $\pm 20\%$ and thus lies within the experimental error bars for the curves shown in Figs. 2, 3, and 4. Another factor which influences the measured intensity at a given photon energy is inelastic scattering of the photoelectrons

during transport to the surface. This effect is most important in just the energy range we have studied.⁹ However, it is difficult to assess and is probably a much weaker effect than the atomic cross section modulation discussed above (the escape depth probably varies by a factor of 2 or less, while the atomic cross section varies over an order of magnitude). We shall therefore consider the variation in mean escape depth to be absorbed in an "effective" cross-section variation.

Strong variations in the photoionization cross section over a small energy range are expected when the initial state wavefunction has at least one node. This may be explained as follows. The selection rules for electric dipole transitions $\Delta l = \pm 1$ connect a d-initial state to p- and f-partial wave final states. In this case the radial dipole matrix element associated with the p or the f channel may change sign as a function of photon energy. The photoexcitation cross section, which is proportional to the sum of the square of the matrix elements, will then exhibit a minimum at the energy for which one of the matrix elements vanishes. Because the absolute value of the d $\rightarrow$ f matrix element dominates the d $\rightarrow$ p one at higher (> 20 eV) energies¹ the minimum observed for Ag 4d at $h\nu = 140$ eV may be attributed to a vanishing d $\rightarrow$ f matrix element at this energy. In contrast to the 4d wavefunction (Ag) which exhibits one radial node the 5d wavefunction (Au, Pt) has two radial nodes. In this case the d $\rightarrow$ f matrix element approaches zero more gradually and the Cooper minimum is smeared out (compare Fig. 3).

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8. X-RAY PHOTOELECTRON SPECTROSCOPIC STUDIES OF THE ELECTRONIC STRUCTURE OF TRANSITION METAL DIFLUORIDES

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Transition-metal compounds are of great scientific and technological interest because they possess a wide range of interesting magnetic and electrical properties. In this paper we report a high-resolution x-ray photoemission (XPS) investigation of several 3d transition-metal difluorides, MnF_2 , FeF_2 , CoF_2 , NiF_2 , and ZnF_2 . The measurements were performed on a modified Hewlett-Packard HP 5950A electron spectrometer, which employs monodromatized AlK α x-rays ($h\nu = 1486.6$ eV) as the photon source. Except for NiF_2 , single-crystal samples were cleaved and studied in ultra-high vacuum. With the aid of previous XPS results from alkali fluorides, the partial 3d densities of states were derived, using the constancy of the F2s-F2p energy separation and relative intensity ratio.

The 3d-metal compounds have spatially localized 3d bands near the Fermi level. The d electrons give rise to the interesting and wide range of properties which characterize these compounds. Because the orbitals in 3d bands do not have a very large spatial extent beyond the ionic cores, they are not greatly broadened by nearest-neighbor overlap. Thus the d-bands are narrow and atomic-like. Photoemission studies of the 3d bands are of particular interest theoretically because the usual band-structure methods that work well for other solids fail to deal with the highly localized (correlated) nature of the 3d electrons. However, simple atomic models have not been completely successful in explaining the properties of these materials, either.

We selected the 3d metal difluorides for study because they are the most ionic and among the simplest of 3d-metal compounds. They are also the most stable, an important factor experimentally. Their electronic structures may provide fiducial marks in understanding the 3d bands in more complicated, more covalent compounds, and may provide a stringent test of electronic structure calculations, in particular for cluster molecular orbital models which have been suggested as being appropriate for these compounds. If these models are successful for the (very ionic) fluorides, they should also be applicable to other 3d metal systems.

Manganese difluoride has a half-filled 3d shell with a $t_{2g}^3 e_g^2$ configuration. The valence region of MnF_2 exhibits two broad peaks, centered at ~ 3.3 eV and 6.6 eV relative to the top of the valence band from ~ 5 to ~ 10 eV. With the aid of the alkali fluoride spectra, we can unambiguously assign the 6.6 eV peak to the F2p band, leaving the peak at 3.3 eV as the 3d bands. Photoionization of a 3d electron in MnF_2 results in either a 5E_g or a $^5T_{1g}$ final state with a relative intensity $(^5T_{1g})/(^5E_g) = 1.5$. We derived a value of 1.0(1) eV for the E_g - T_{1g} splitting by fitting our data with this ratio. Multiple scattering X α (MSX α) calculations of Larsson and Connolly¹ on a MnF_6^{4-} cluster gave 1.36 eV for the splitting. Recently Viinikka and Bagus² have performed calculations on transition-metal fluoride

clusters using a multiconfigurational Hartree-Fock (MCHF) treatment. This *ab initio* treatment yields a 1.1 eV separation between the 5E_g and $^5T_{1g}$ final states of MnF_6^{4-} , in better agreement with experiment. In the spectral region to higher binding energy from the Mn 3d and F2p peaks is some intensity which is not accounted for by either the p- or d-bands. This intensity is probably due to correlation ("shake-up") states, which are well-known in core-level spectra of transition metal compounds.³⁻⁵ Correlation states derived from ligand-to-metal charge transfer are predicted in this region by the MCHF calculation.

The valence-band spectrum of FeF_2 is very similar to MnF_2 except for a new, well-resolved peak at the top of the valence band. The new peak (at 2.0 eV) is due to final-state multiplets. Photoemission from $Mn^{+2}(3d^5)$, with a half-filled d shell, can only lead to quintet final states. In $Fe^{+2}(3d^6)$, the one extra d electron is antiparallel to the other majority-spin d electrons. Thus both quartet and sextet final states are possible. A large peak centered at 5.1 eV represents the manifold of quartet states, and the peak at 2.0 eV, with about 1/5 the intensity, is the 6A_1 final state. A similar conclusion was drawn by Wertheim, et al.⁶ from a spectrum in which the 6A_1 state was just resolved. This emphasizes the very localized nature of the 3d bands.

The VBDOS of CoF_2 (Fig. 1) is not as simple as those of MnF_2 or FeF_2 . However, our success in us-

Fig. 1. The XPS valence-band spectrum of CoF_2 . (XBL 757-3458A)

ing the LiF data to decouple the F2p contribution from the 3d states in the simpler cases of MnF_2 and FeF_2 gives us confidence to apply this technique to CoF_2 . The results are shown in Fig. 2. Also shown in Fig. 2 as lines are the most intense final states predicted by the MCHF calculation of Viinikka and Bagus.² The agreement is remarkably good. The hatched area represents correlation-state structure, which is much more intense than in FeF_2 or MnF_2 . However, Co core levels of CoF_2 also exhibit in-

tense correlation-state satellites, while in MnF_2 and FeF_2 the metal core levels have much weaker satellites.⁴ The MCHF calculation predict correlation states in this region, as indicated in Fig. 2.

Fig. 2. The partial d-density of states of CoF_2 , obtained as discussed in text. The solid vertical bars represent calculated d-states from MCHF calculations of Ref. 2. Hatched area represents mostly shake-up intensity. The horizontal bar represents the region of predicted shape-up from Ref. 2.

(XBL 762-2317)

The XPS valence-band spectrum of NiF_2 , like CoF_2 is not very simple, as there is a large degree of overlap between the metal 3d bands and the F2p bands. We do find good agreement with both the (polycrystalline) XPS spectrum of Wertheim, et al.⁶ and the UPS work of Poole and co-workers⁷ at $h\nu=40.8$ eV on NiF_2 . Again very reasonable agreement with MCHF calculation for the 3d states is observed after subtracting out the F2p contributions.

In conclusion, we found the metal 3d bands and fluorine 2p bands to be decoupled in the transition-metal difluorides. For cases in which MCHF cluster calculations are available (MnF_2 , CoF_2 , NiF_2), these calculations were found to predict both the d-band structures and the energies of the correlation states very well. Thus the cluster model appears useful when applied to transition-metal compounds.

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9. AN X-RAY PHOTOEMISSION INVESTIGATION OF THE DENSITY OF STATES OF β' -NiAl

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During the past decade there has been much progress in the development of band-structure calculations for alloys. Similarly, experimental techniques for characterizing alloy band structure are also still evolving. In this report we have used x-ray photoemission spectroscopy (XPS) to answer one fundamental question about a simple alloy: the filling of the nickel d-bands in NiAl.

The Engel-Brewer theory of alloys as well as more sophisticated theories support the concept of a filled d-band in NiAl.^{1,2} For an understanding of the electronic structure of this alloy XPS may be the method of choice because it should yield the initial-state density with some reliability as well as probe atomic core-levels.

NiAl is a member of the class of alloys which form β' -phases at approximately 50-50 atomic per cent. These alloys have the CsCl crystal structure and are ordered at room temperature. For the Ni-Al system this phase exists between 40 and 55 atomic per cent of Al.

Fig. 1. Valence band density for β' -NiAl. Points are the experimental XPS results (this work) and the dashed curve is from calculations of Connolly and Johnson (Ref. 2). (XBL 7410-4352A)

Figure 1 shows the XPS-VB DOS which was obtained for β' -NiAl. It is compared with the calculated density of states of Connolly and Johnson² using the (nonrelativistic) Augmented-Plane-Wave (APW) method in conjunction with an LCAO interpolation scheme. Inspection of Fig. 1 shows first that the VB DOS is not a superposition of the VBOS's of pure Al metal and pure Ni metal.³ Secondly, the general shape of the VB DOS agrees well with the calculated VB DOS of Connolly and Johnson² and the more recent KKR results of Morruzzi, Williams, and Janak.⁴ The latter authors examined the effects of alloying on total band width by means of KKR calculations on a series of (CsCl type) intermetallics and found in general a band narrowing in these systems. This narrowing can result from either 1) a lack of d-density of final states on neighboring atoms onto which electron tunneling can occur or 2) mutual d-band repulsion. The latter mode is of course not operative in the NiAl case because only one of the components has d-bands. For NiAl we obtain a band narrowing N^5 (relative to Ni metal) equal to 0.06 as opposed to 0.33 given by Morruzzi, et al. This comparison is not strictly valid because Morruzzi, et al. are using a hypothetical diatomic Ni moiety as a reference and we are using Ni metal. In the case of β -brass (CuZn), we obtain, using the recent results of Wertheim, et al.,⁶ a value $N = .11$ (relative to Zn metal) and $N = .13$ (relative to Cu metal) as opposed to 0.82 (relative to Zn₂) and 0.66 (relative to Cu₂). The predicted results are again far from the observed values but NiAl is predicted to have N about half as large as β -brass, as observed.

By carrying their calculations to self-consistency, Morruzzi, et al. were able to compute charge densities and discuss charge transfer, which is related to the question of the occupancy of the d-bands. Several experimental results suggest that Al 3s electrons are transferred to Ni and fill or very nearly fill the d band.⁷ This might seem to be easily determined by measuring the "chemical shift" of NiAl core lines with respect to the pure metals. However, there appears to be no shift in the Al lines and only small shifts in different directions for the various Ni lines. In general large shifts in metals haven't been observed because of opposing effects—"charge transfer" vs. relaxation.⁸ The implications of the Ni line positions are not clear because multiplet effects may cause a shift in the spectral weight. Filling of the d band should greatly reduce the relaxation because of the loss of d-wave screening. This effect should be most pronounced in the Auger spectrum where there is a two-hole final state. Again no large shift is observed and qualitatively the spectra look similar.

The effect of a filled d-shell would be the absence of the multiplet structure on the Ni core levels in NiAl as opposed to Ni metal. The Ni 3s level is considerably more symmetric in NiAl than in Ni metal and is significantly narrower (by 0.7 eV). The full-widths at half-maximum (FWHM) of the various levels in NiAl and Ni and Al metals are tabulated in Table 1. The Al levels are nearly the same in the alloy as in the metal, while all the Ni lines are considerably narrower in the alloy.

The 2p levels of Ni in paramagnetic compounds show intense satellites (with as much as 50% intensity of the primary peak) at higher binding energy,

Table 1. Comparison of FWHM of core-levels in NiAl, Ni and Al.

	metal		NiAl ^b		metal	
	Ni ^a	Ni	Al	Al	Al ^c	Al
2s	---	---	1.17(5)	1.25(5)		
2p _{1/2}	1.9	1.6	.86	.95		
2p _{3/2}	1.6	1.3				
3s	3.2	2.5	---	---		
3p	3.6	3.2	---	---		

a) Unpublished data.
b) This work.
c) Unpublished data.

while compounds with diamagnetic Ni and Cu, with a filled d-band, do not show this satellite structure.⁹ Ni metal itself exhibits readily observable satellites with approximately 10% the intensity of the primary peak. In NiAl the 2p satellites are very weak or absent (Fig. 2). This observation supports a filled d-band hypothesis in NiAl.

Fig. 2. Ni 2p spectrum from β' -NiAl.
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10. THE ELECTRONIC STRUCTURE OF SrTiO₃ AND SOME SIMPLE RELATED OXIDES

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Strontium titanate crystallizes in the simple cubic perovskite structure. Its properties range from exhibiting ferroelectricity to becoming a superconductor at low temperatures. The perovskites have been studied with a wide range of experimental techniques. We have studied SrTiO₃ with x-ray photoelectron spectroscopy (XPS) under UHV conditions and with high resolution, to elucidate its total valence-band density of states (VB DOS). In order to help understand the SrTiO₃ spectra, we have also studied simple related oxides; MgO, ZnO, Al₂O₃, TiO₂, and SrO, which are discussed first.

Magnesium oxide crystallizes in the NaCl structure. The XPS spectrum of its outermost levels is shown in Fig. 1. The valence bands consist of three groups of peaks. One, at about 18 eV from the top of the valence band, can be assigned to the O2s levels. A broad two-peak structure due to the O2p-Mg3s bands extends from about 0 to 6.5 eV relative to the top of the valence bands. We will refer to this entire two-peak structure as the valence bands.

Fig. 1. XPS spectrum of the outermost levels in MgO. (XBL 757-3398)

There are several calculations available on the electronic structure of MgO. Tossell carried out SCF $X\alpha$ scattered wave calculations on MgO_6^{10-} clusters. He predicted the valence levels to fall into three sets. There are $5a_{1g}$, $4t_{1u}$, and $1e_g$ levels which are O2s nonbonding orbitals, then a set of bonding orbitals which are predominantly O2p ($5t_{1u}$, $6a_{1g}$, and $1t_{2g}$), and finally a set of nonbonding O2p orbitals ($1t_{2u}$, $6t_{1u}$, $2e_g$, and $1t_{1g}$). The oxygen 2s levels are predicted to be about 1 eV wide, which agrees well with the observed FWHM of this peak. The top two bands have an observed bandwidth of 6.5 eV. The calculated bandwidth of 3 eV is too small, as might be expected from a MO calculation. Tossell's calculation¹ gives ~1.8 eV for the separation between the two groups of O2p bands, which compares with our measured separation of 2.5 eV. The separation between the O2s and the O2p bonding band is calculated to be 12.5 eV, while our results for the separation of the O2s band from the more tightly-bound valence band is measured to be 14 eV. Thus Tossell's calculation gives quite reasonable agreement with experiment. Several band-structure calculations are also available. In general they do not agree so well.

Fischer has reported x-ray emission (XES) studies² of MgO as have Fomichev, et al.³ Fischer's spectra yield a bandwidth of about 7 eV ($MgK\beta$), a band splitting of ~2 eV (in both $MgK\beta$ and OK spectra) and the O2s levels at 14.5 eV ($MgK\beta'$ - $MgK\beta$ separation) above the bottom valence band. Thus there is quite good agreement between the XPS and XES results.

The valence band spectrum of Al_2O_3 is qualitatively very similar to that of MgO. There is a two-peak valence band structure plus the more tightly bound peak due to the O2s band. There is also quite good agreement with the x-ray emission results. The separation of the two peaks in the valence band is somewhat smaller in the XES spectrum than in the XPS spectrum. This difference is due most likely to matrix element effects enhancing different parts of the valence band in the two experiments.

Two $MSX\alpha$ cluster calculations have been reported.^{1,4} They however do not agree well with each other. Tossell's calculation is in better agree-

ment with our experiment. However, as in the case of MgO, Tossell's calculation gives a valence bandwidth narrower than experiment. The total valence bandwidth from the XPS data is approximately 26 eV, while XES give a bandwidth of ~27 eV.² This compares to the theoretical value from MSX calculations of 16 eV. The band structure calculation of Douglas also gives a bandwidth of about 16 eV.⁵

Strontium oxide has been studied relatively little. The XPS spectra are expected to be qualitatively similar to MgO, which is the case. In SrO, the $Sr4p$ core level overlaps the O2s band. The bandwidth in SrO is about 10 eV and the splitting is about 4.5 eV, both surprisingly somewhat larger than what was observed in MgO. There are no detailed calculations for SrO. The SrO results will be useful primarily in helping to interpret the levels due to Sr in the $SrTiO_3$ spectra.

There appear to have been no band-structure calculations for TiO_2 . However, Tossell, et al.⁶ performed MO calculations using the SCF $X\alpha$ method for TiO_6^{8-} and there have been several band-structure calculations on TiO ^{7,8} and one for Ti_2O_3 .⁹ The TiO_2 VBDOS is very similar to what was observed for MgO. There are two peaks in the valence band, separated by 1.9 eV. The total bandwidth is 5.5 eV. The more tightly bound O2s level has a FWHM of 2.5 eV, and lies 15.0 eV higher than the lower valence-band peak. This agrees fairly well with the MO cluster calculation of Tossell, et al. The $X\alpha$ calculation has a roughly 2-eV wide O2s nonbonding band ($5a_{1g}$, $4t_{1u}$, and $1e_g$) which is about 11.5 eV more tightly bound than the bonding orbitals ($5t_{1u}$, $6a_{1g}$, and $1t_{2g}$) which are predominantly O2p. These bonding orbitals are separated from the nonbonding orbitals by 3.0 eV. The total valence bandwidth is about 5.5 eV. While we cannot make direct comparison with a TiO_2 band structure, band structure results for TiO and Ti_2O_3 yield bandwidths of ~4.5 eV and separation of O2s to O2p of 14 to 14.5 eV.^{7,9}

The $SrTiO_3$ VBDOS is expected to resemble that of TiO_2 , because in both cases Ti is octahedrally coordinated to oxygen. Optical properties and soft x-ray emission spectra of these two materials have been shown to be very similar. Our XPS spectrum, shown in Fig. 2, is indeed similar to that of the oxides discussed above. The O2s band overlaps with the $Sr4p$ band, but from relative intensity arguments the high binding-energy shoulder is probably the O2s band. The p bands are 6.5 eV wide. There appear to be several features in the VBDOS but details of these features will have to await higher resolution studies. Two major features, separated by 1.9 eV, are resolved in the valence bands. The O2s band is separated from the 4.5 eV feature by ~14.5 eV.

Theoretical studies include band-structure calculations by Kahn and Leyendecker¹⁰ (LCAO-tight binding), Mattheiss¹¹ (APW), Soules, et al.¹² (ab initio-SCF-LCAO, also a cluster calculation was performed by these authors) and Wolfram, et al.¹³ (LCAO). Kahn and Leyendecker calculated only the p bands for $SrTiO_3$. Their calculation determined the bandwidth to be 4.5 eV. The calculations of Wolfram, et al. yielded a bandwidth of 4 to 4.5 eV. Soules et al. calculated the bandwidth to be 5.86 eV; however, their calculated O2s bandwidth of 5.2 eV is much too large. Mattheiss' calculations give a bandwidth of

Fig. 2. XPS spectrum of the outermost levels in SrTiO₃ (upper panel); XPS spectrum of the valence region of SrTiO₃ (lower panel). (XBL 757-3396A)

3.5 - 3.8 eV, with about 2.0 separation of the principal features in the density of states. His O2s band is about 1 eV wide and ~14.8 eV above the valence band. Soules, et al. also carried out a calculation on an isolated TiO₆⁸⁻ cluster which gave fairly similar results to their band structure calculation, with the valence band being wider by about 2 eV (i.e., ~8 eV wide). This result, along with the similarity of SrTiO₃ and TiO₂ XES spectra, suggests that short range order is an important factor in determining the VB DOS of these materials.

In summary, the XPS spectra of SrTiO₃ and several related oxides yield the total VB DOS of these materials. The electronic structures are now well understood, at least on a gross scale. Among the various electronic structure calculations now available, cluster-type models give the best agreement with experiment.

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11. FLUORESCENCE LIFETIME MEASUREMENTS OF $np^5(n+1)s^1$ STATES IN KRYPTON AND XENON

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Synchrotron radiation from the Stanford storage ring (SPEAR) has been used to excite the lowest atomic states in Xe and Kr and study their fluorescent decay rates. The light pulses of SPEAR have a width of 0.4 ns, and the time interval between consecutive pulses is 780 ns. This time structure is very favorable for measuring radiative lifetimes of atomic and molecular states in particular in the far UV where there are no laser pulses or fast electro-optical shutters available.

Oscillator strengths for the $np^5(n+1)s^1$ levels in Xe and Kr have been the subject of investigation by several methods, and the various results are not always mutually consistent (see Tables 1 and 2). The most direct method for lifetime determinations, the observation of the fluorescent decay following pulsed resonance excitation had not been used before because of lack of a proper light source. Lifetime measurements of the $np^5(n+1)s^1$ states in rare gases are of interest for several reasons. For Kr and Xe, the large spin-orbit splitting of the core hole state requires an alternative coupling scheme. Therefore, reliable experimental values should be available to test various theoretical approaches. Another point is that the atomic decay rate constants enter significantly the rate equations describing the formation of the various excited states.

Experimentally we used a gas vessel, sealed by a LiF-window against the ultrahigh vacuum of the storage ring, and two EMR 541-G 12-stage photomultipliers, equipped with a LiF-window and a CsI cathode, mounted perpendicular to the photon beam to record the fluorescence radiation. These PM tubes limited the time-resolution of the apparatus to about 1.8 ns.

Table 1. Compilation of lifetimes and oscillator strengths for the two transitions $^3P_1 \rightarrow ^1S_0$ and $^1P_1 \rightarrow ^1S_0$ in KRYPTON.

$^3\tau$ (ns)	3f (1236Å)	$^1\tau$ (ns)	1f (1165Å)	Method	Authors
4.14	0.166			resonance imprisonment	Turner ¹ (1965)
4.32±0.33	0.159±0.01	4.52±0.35	0.135±0.01	total absorption	Wilkinson ³ (1965)
3.3 ±0.8	0.21 ±0.05	2.9 ±0.7	0.21 ±0.05	linear absorption	Chashchina and Shreider ⁶ (1966)
3.37±0.33	0.204±0.020	3.32±0.36	0.184±0.020	optical line broadening	Vaughn ⁷ (1968)
3.67±0.12	0.187±0.006	3.16±0.15	0.193±0.009	total absorption	Griffin and Hutcherson ⁹ (1969)
4.0 ±0.8	0.173±0.035	3.5 ±0.7	0.173±0.035	electron energy loss	Geiger ¹⁰ (1970)
		4.2 ±0.4	0.142±0.015	self-absorption	de Jongh and van Eck ¹² (1971)
3.2 ±0.1	0.208±0.006	3.1 ±0.1	0.197±0.006	resonance fluorescence	present work
4.98	0.138	4.49	0.136	nonrel. Hartree-Fock	Dow and Knox ¹⁵ (1966)
3.43	0.20	3.05	0.20	intermediate coupling	Gruzdev ¹⁶ (1967)
3.61	0.190	3.45	0.177	calc. multiple conf. appr.	Gruzdev and Loginov ¹⁷ (1975)

Table 2. Compilation of lifetimes and oscillator strengths for the two transitions $^3P_1 \rightarrow ^1S_0$ and $^1P_1 \rightarrow ^1S_0$ in XENON.

$^3\tau$ (ns)	3f (1470Å)	$^1\tau$ (ns)	1f (1296Å)	Method	Authors
3.79 ±0.12	0.256±0.008	3.17±0.19	0.238±0.015	zero field level crossing	Anderson ² (1965)
3.5 ±0.6	0.28 ±0.05	3.3 ±0.7	0.23 ±0.05	linear absorption	Chashchina and Shreider ⁵ (1966)
3.74 ±0.25	0.260±0.020	2.80±0.20	0.270±0.020	total absorption	Wilkinson ⁴ (1966)
		3.89±0.10	0.194±0.005	total absorption	Griffin and Hutcherson ⁹ (1969)
3.73 ±0.75	0.260±0.052	4.0 ±0.8	0.190±0.038	electron energy loss	Geiger ¹⁰ (1970)
3.57	0.272	3.99	0.189	low-energy electron impact	Lu ¹¹ (1971)
4.6 ±0.5	0.213±0.020	4.2 ±0.9	0.180±0.040	resonance imprisonment	Wieme and Mortier ¹³ (1973)
5.31	0.183	4.47	0.169	low-energy electron impact	Delage and Carette ¹⁴ (1976)
3.5 ±0.1	0.263±0.007	3.4 ±0.1	0.229±0.007	resonance fluorescence	present work
5.00	0.194	5.13	0.147	nonrel. Hartree-Fock	Dow and Knox ¹⁵ (1966)
3.47	0.28	3.02	0.25	intermediate coupling calc.	Gruzdev ¹⁶ (1967)
4.58	0.212	3.99	0.189	nonreal. Hartree-Fock	Kim et al. ⁸ (1966)

The absorption spectrum was monitored by a sodium salicylate-RCA 8850 detector combination. There was no energy selective device in the fluorescence channel since in atomic systems at low pressure only resonance fluorescence occurs. The acceptance range for fluorescence was 1050-1850 Å due to the

LIF-cutoff and the CsI response. Within the region in Kr only the spin-orbit doublet of the $4p^55s^1$ configuration could be excited, while in Xe the analogous levels plus several more states could be reached. A typical absorption and fluorescence spectrum for Xe at 10 Torr is shown in Fig. 1.

Fig. 1. Absorption and fluorescence spectra of Xe.
(XBL 766-2949)

Lifetime measurements have to be carried out in the 10^{-5} - 10^{-6} Torr pressure range to avoid any background from resonance trapping. In Fig. 2 a

Fig. 2. Fluorescence decay curves of Kr.
(XBL 7612-4534)

characteristic result for the exponential decay of the $4p^5(2p_{3/2})5s J=1$ and $4p^5(2p_{1/2})5s J=1$ states of Kr at 3×10^{-6} Torr is displayed. Even at these low pressures there is a finite probability that resonance scattering occurs on the way between the fluorescence volume and the detector. Obviously,

such a process results in an apparent lifetime longer than the true one. Barrat¹⁸ gives an expression for this ratio which, at low pressures, can be approximated by the linear dependence.

$$\frac{\tau}{T} = 1 - \alpha \sigma n L$$

where τ stands for the true and T for the apparent lifetime. σ is the resonance cross section, n the density, and L the dimension of the cell. To obtain the true lifetime, the pressure dependence must be measured and extrapolated to zero pressure. Figures 3 and 4 show this procedure for the $3p_1$ and $1p_1$ states of Kr and Xe, as well as for the $5p^5(2p_{3/2})5d J=1$ state in Xe which has not been measured before.

Fig. 3. Lifetimes vs. pressure for Kr:

- 5s(3/2) 1
 - 5s(1/2) 1
- (XBL 7612-4529)

A comparison of our results with previous data and theoretical predictions are given in Table 1 for krypton and Table 2 for xenon. The large scatter as well as the large limits of error of the indirect methods emphasize the need for a direct lifetime measurement. An exception is the zero field level crossing measurement by Anderson² in Xe which we consider to be the most reliable set of existing data. Our result is in excellent agreement with the values given by Anderson.² Comparing our experimental result with theoretical predictions, the nonrelativistic HF calculations of Dow and Knox¹⁵ are badly off, whereas the scheme of Gruzdev^{16,17} seems to describe the measured data quite well.

The lifetime of the $5p^5(2p_{3/2})5d J=1$ state at 1192 Å was determined in the same manner. The result $\tau = 1.4 \pm 0.2$ ns reflects the large oscillator strength of this transition. There are no theoret-

Fig. 4. Lifetimes vs. pressure for Xe:

● 6s(3/2)1
 ■ 6s(1/2)1
 ▲ 5d(3/2)1 (XBL 7612-4532)

ical predictions available for comparison. Calculations of Gruzdev and Loginov¹⁷ however, yield for the lifetime of the analogous state in krypton a value of 1.87 ns which confirms the trend observed in xenon.

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12. ZEEMAN BEATS IN THE RESONANCE FLUORESCENCE OF THE 3P_1 STATES IN KRYPTON AND XENON

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The quantum-beat method offers a way of measuring the fine structure or hyperfine structure splittings of excited states. Frequencies can be determined within limits set by the time resolution of the apparatus and by the excitation mechanism. The time structure of light pulses from the storage ring SPEAR (width 0.4 ns, repetition time 780 ns) permits the measurement of interaction frequencies in the range from a few MHz to about 1 GHz. Here we report about an attempt to demonstrate the applicability of synchrotron radiation for Zeeman beat experiments.

Primary conditions for the observation of interference effects in the decay of neighboring states are: (1) The states must be coherently (in time) populated such that there exists a well-defined phase relation in the time evolution of these states. According to $\Delta E \cdot \Delta t \gtrsim \hbar/2$, this condition requires short light pulses, and their width sets an upper limit to the observable splitting. (2) The splitting, to be observed in form of a modulation frequency, should not be energetically resolved by the radiation detectors. (3) If the interference is to be detected via polarization or angular anisotropy the emitting state must be polarized or aligned, respectively.

The formalism to describe these interference effects can be found in several references.¹ Usually, the same phenomenon is treated differently depending on whether the problem belongs to atomic or nuclear spectroscopy. We adopt here the notation of Ref. 2. If $\underline{k}_1$ is the direction of the primary photon beam, the intensity of the fluorescent light along the direction $\underline{k}_2$ at time t after the excitation can be expressed as

$$W(\underline{k}_1, \underline{k}_2, t) = \text{Tr}[\rho(\underline{k}_1, t) \epsilon(\underline{k}_2)]. \quad (1)$$

Here, $\rho(\underline{k}_1, t)$ is the density matrix describing the ensemble of excited states, and the efficiency matrix $\epsilon(\underline{k}_2)$ characterizes the detector system. In terms of statistical tensors Eq. (1) can be written

$$W(\underline{k}_1, \underline{k}_2, t) = \sum_{q, \lambda} \rho_{\underline{k}_1}^{\lambda}(t) \cdot \epsilon_q^{\lambda}(\underline{k}_2). \quad (2)$$

Synchrotron radiation is linearly polarized and resonance absorption prepares the excited ensemble in a strongly oriented (polarization and alignment) state, which means $\rho_{\underline{k}_1}^{\lambda}$ has no rotational symmetry about $\underline{k}_1$ at $t=0$. If the detector system is polarization-sensitive the same statement applies to ϵ_q^{λ} .

with respect to $\underline{k}_2$. In the case reported here, however, the detectors were not sensitive to linear polarization and hence the efficiency tensor was rotationally symmetric about $\underline{k}_2$. This implies that only terms with $q=0$ contribute and Eq. (2) simplifies accordingly. Since only dipole radiation contributes, λ will be restricted to 0 and 2. The application of a magnetic field (z-axis) perpendicular to $\underline{k}_2$ (see Fig. 1) mixes the states with re-

The transformation of the representation from $\underline{k}_1$ into the z-axis is described by the rotation group $D_{\infty h}(\lambda)(\underline{k}_1 \rightarrow \underline{z})$. A detailed calculation of Eqs. (2) and (3), as carried through in Ref. 2, leads to a simple periodic modulation of the fluorescence intensity

$$W(\theta, t) = A_0 e^{-t/\tau} [1 + A_2 P_2(\cos(\theta - \omega_0 t))]. \quad (4)$$

Here, θ is the azimuthal angle between $\underline{k}_1$ and $\underline{k}_2$. The modulation amplitude A_2 is determined by the multipolarity (E1) of the radiation and by the total angular momentum of the initial and final states of the transition.

The principal layout of the experimental setup is shown in Fig. 1. The gas pressure in the chamber was reduced as much as was permissible intensity-wise. In Figs. 2 and 3 the modulated decay of the 3P_1 states in Kr and Xe, respectively, is shown for two magnetic fields. The two corresponding frequencies can clearly be distinguished. The obviously different modulation amplitude in Kr and Xe is a result of the hyperfine interaction in the abundant isotopes Xe-129 and 131. As outlined in Table 1 all even-even isotopes with nuclear spin $I=0$ have the same frequency in an external field. In krypton this includes 88.5% of all isotopes but in xenon only 52.4%. In addition, it can be seen from Table 1 that the Zeeman-frequencies of the hyperfine components in Kr-83 are small compared to the dominant gJ-frequency. This is not the case in xenon where the Zeeman-frequencies of the hyperfine levels in Xe-129 and 131 are quite comparable to or even larger than

Schematic of experimental apparatus

Fig. 1. Schematic of experimental apparatus.
(XBL 7612-11128)

spect to this representation and the density tensor becomes time-dependent

$$\rho_{\underline{k}_1}^{\lambda}(t)^* = \sum_{\lambda, q'} \rho_{q'}^{\lambda}(0)^* \cdot e^{-iq'\omega_0 t} \cdot D_{q'0}^{(\lambda)*}(\underline{z} \rightarrow \underline{k}_1), \quad (3)$$

where $\omega_0 = g_j \frac{\mu_B}{\hbar} H_0$ is the (Larmor) interaction frequency.

Table 1. Zeeman-frequencies of various isotopes in krypton and xenon.

Kr isotopes	78	80	82	83			84	86
abundance (%)	0.35	2.25	11.6		11.5		57	17.3
ang. momentum	J=1	J=1	J=1	$F=\frac{11}{2}$	$F=\frac{9}{2}$	$F=\frac{7}{2}$	J=1	J=1
g-factor	1.242	1.242	1.242	0.226	0.050	-0.276	1.242	1.242
v in MHz for								
H _O = 40 G	69.53	69.53	69.53	12.65	2.80	15.45	69.53	69.53
H _O = 28 G	48.67	48.67	48.67	8.86	1.96	10.82	48.67	48.67

Xe istopes	124	126	128	129	130	131			132	134	136	
abundance (%)	0.10	0.09	1.9	26.4	3.9		21.2		27.0	10.5	8.9	
ang. momentum	J=1	J=1	J=1	$F=\frac{3}{2}$	$F=\frac{1}{2}$	J=1	$F=\frac{5}{2}$	$F=\frac{3}{2}$	$F=\frac{1}{2}$	J=1	J=1	J=1
g-factor	1.204	1.204	1.204	0.803	1.605	1.204	0.482	0.321	-0.80	1.204	1.204	1.204
v in MHz for												
H _O = 40 G	67.40	67.40	67.40	44.94	89.87	67.40	26.96	17.98	44.94	67.40	67.40	67.40
H _O = 28 G	47.18	47.18	47.18	31.46	62.91	47.18	18.87	12.58	31.46	47.18	47.18	47.18

Fig. 2. Quantum beats of Kr 5s[3/2]1 state.
(XBL 7612-4533)

Fig. 3. Quantum beats of Xe 6s[3/2]1 state.
(XBL 7612-11129)

the g_J -frequency in the $J=1$ state of the even-even isotopes. This superposition of frequencies in xenon attenuates the modulation amplitude and leads to the effect shown in Fig. 3. In contrast, for krypton clearly one frequency is dominant.

The observed frequencies agree to the accuracy obtained with the g_J -factors taken from Moore's compilation.³ The application of higher external fields would lead to a greater accuracy for the g_J -value, but it should be noted that the time-resolution of our detectors sets an upper limit of about 60-80 G for the magnetic field strength.

This technique can be successfully applied to investigate g_J -factors of higher-lying states in noble gases, in particular xenon. It is by no means, however, restricted to atoms and applications toward VUV transitions in polyatomic molecules is expected.

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13. LIFETIME MEASUREMENTS OF RARE-GAS DIMERS

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There has been a great deal of recent interest in the electronically excited rare-gas dimers as they represent potential UV lasing systems.¹ For the continued development of these lasers, the detailed nature of the dynamics and mechanisms of the lasing transitions are essential. For this purpose, we have measured the radiative decay lifetimes of the low-lying electronic states of the Xe_2^* molecule utilizing the pulsed synchrotron radiation from the Stanford Positron-Electron Accelerator Ring (SPEAR). The synchrotron radiation from SPEAR serves as an ideal source for these measurements for two reasons: 1) the oscillation period of 780 nsec permits measurement of short and moderately long lifetimes; 2) the short pulse duration (0.4 nsec) is short enough that the ultimate time resolution is due entirely to the detector's response function.

Fig. 1. Schematic representation of experimental apparatus.
(XBL 7612-4530)

The experimental apparatus and associated electronics are shown in Fig. 1. The synchrotron radiation is dispersed by a Seya-Namioka monochromator (GCA/McPherson, UHV design) and enters the sample chamber through a LiF window. The fluorescent radiation is detected perpendicular to the beam axis without energy discrimination.² The Xe pressure in these measurements ranged from 2 to 200 Torr.

The decay curve is generated by a photon coincidence technique whereby the time between the initial excitation pulse and a single fluorescence photon event is measured. This time is measured by a time-to-amplitude converter (TAC), and stored in a multi-channel analyzer operating in the pulse height mode.

To extract a lifetime from these data, the "prompt", or Rayleigh scattering contributions to the decay curve must be considered. Since these effects become less important at longer times, the curve-fitting was done by fitting only that part of the decay curve far from the prompt.

The fluorescence decay curve at 20 Torr and 1470 Å excitation wavelength is seen to consist of a short- (Fig. 2) and a long-lived (Fig. 3) component. The measured lifetimes of these components are 1.6 ± 0.1 and 105 ± 1 nsec, respectively. The values of these lifetimes are found to be dependent on excitation wavelength and sample pressure, showing variations of less than $\pm 20\%$.

Fig. 2. Decay curve of $O_u^+ Xe_2^*$ states. (XBL 766-2947)

We have noted that the long component becomes more intense relative to the short lifetime as the excitation wavelength exceeds 1500 Å. In addition, when the excitation wavelength is held at 1475 Å and the Xe pressure is increased, the long component again becomes more intense relative to the short component.

These results are easily understood when interpreted in the frame-work of Fig. 4. The fluorescence decay observed results from transitions from the lowest bound excited states of Xe_2^* to the repulsive wall (~ 1720 Å) of the ground state. Of the three bound low-lying states (O_u^+, O_u^-, I_u), only the

Fig. 3. Decay curve of $I_u Xe_2^*$ and $O_u^+ Xe_2^*$ states (note contracted time scale). (XBL 7612-11055)

Fig. 4. Energy level diagram of the lowest lying states of Xe_2^* and $Xe_2(XO_u^+)$ (adapted from Fink and Comes, Ref. 5). (XBL 7612-4531)

O_u^+ and the 1_u can undergo allowed transitions to the ground state, O_g^+ .⁵ The 1_u state is expected theoretically to have a long lifetime since the dissociation limit of this state is metastable, i.e., $^3P_2 + ^1S_0$ Xe atoms.⁵

At an excitation wavelength of 1470 Å, the Xe_2 ground state molecules are excited to the high vibrational levels of the O_u^+ state (Fig. 4). On the basis of the above theoretical arguments, we assign the short component to the O_u^+ state and the long-lived component to the 1_u state. This is consistent with the observation that the relative intensity of the short component to the long component decreases as the excitation wavelength is increased.

The O_u^+ state has a nominal lifetime of 1.6 nsec; the variation of the lifetime with excitation wavelength and pressure is interpreted as a result of oscillator strength dependence on the vibrational state.

At a pressure of 20 Torr the $Xe_2(O_u^+)$ molecule has a finite probability for collision with a Xe atom⁴ resulting in T-V energy transfer.⁵ The collision can also induce an intersystem crossing event such that the molecule will be found in the 1_u electronic state after the collision. It is apparent that this process is responsible for populating the 1_u state, whose decay is observed even at 1470 Å excitation wavelength.

There have been many conflicting values reported by other investigators of the O_u^+ lifetime.⁶⁻¹⁰ These previous measurements of Xe_2 lifetimes have been done using pulsed electron bombardment of high pressure Xe gas. In contrast to the monochromatic photon absorption experiment which excites to specific upper levels, high energy electron bombardment, e.g., 160 kV,⁶ creates molecules in many highly excited electronic states. Measured lifetimes from these experiments would be convoluted by effects of cascading and direct fluorescence from the upper excited state to the lower-lying states. Because of inherent difficulties associated with the electron excitation measurements, we believe that the lifetimes reported here are the most realistic estimates for the 1_u and O_u^+ states to date.

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2. Without energy discrimination, cascading events cannot be monitored directly; however, they can be detected indirectly, i.e., nonexponential decay curves. We detect all photons with $1050 \text{ Å} \leq \lambda \leq 1800 \text{ Å}$.

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14. CONFIGURATION INTERACTION EFFECTS IN THE ATOMIC PHOTOELECTRON SPECTRA OF Ba, Sm, Eu, and Yb

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Recent theoretical analyses^{1,2} have been made of the manner in which electron correlation can lead to satellite peaks in photoelectron spectra. There are four mechanisms that describe the breakdown of the one-electron picture: initial-state configuration interaction (ISCI), final-ionic-state configuration interaction (FISCI), continuum-state configuration interaction (CSCI), and autoionization. Among these four mechanisms, autoionization is easily distinguishable because of its resonant nature. The distinction among the other three is not so straightforward; indeed this distinction is unique only within the context of a particular basis set used in configuration interaction. Nevertheless, in certain atomic cases, ISCI can be regarded as the sole dominant contributor to the satellites simply on the grounds of symmetry and near-degeneracy of states. Particularly in the cases where the distinction of the mechanisms can be made, satellite structure can provide unique information about the nature and extent of electron correlation effects.

Recently we³ reported the observation of ISCI satellites in the photoelectron spectra of Group IIA and IIB elements. Furthermore, in the HeI photoelectron spectrum of Ba,⁴ autoionization was revealed by the remarkably high intensities of the satellite peaks. Continuing our work with metal vapors, we have made a similar study on some lanthanides, i.e., Sm, Eu, and Yb. We now wish to present a complete report on the spectrum of Ba and also the observation of satellites in the UV photoelectron spectra of Sm, Eu, and Yb. By analysis of the spectra excited by the various He and Ne resonance lines, satellites due to ISCI and autoionization have been differentiated.

The photoelectron spectra of Ba, Sm, Eu, and Yb are displayed respectively in Figs. 1-4, with the assignments of the prominent peaks labeled. The peaks marked S are due to photoemission induced by HeI or NeI satellite lines and those denoted I are inelastic loss peaks of the intense lines involving the $6s \rightarrow 6p$, $\Delta S=0$ and $\Delta L=1$ transitions. The states and relative intensities for these spectra are correspondingly tabulated in Tables 1-4. The temperatures at which the spectra were recorded are: Ba/HeI (620°C), Ba/NeI (700°C), Sm/HeI (640°C),

Fig. 1. Photoelectron spectra of Ba^+ . (a) Excited by HeI lines. The peaks marked S are due to ionization by the HeI β lines. (b) Excited by NeI lines. The peaks marked S_1, S_2 , and S_3 are due to ionization by the more energetic NeI satellite lines, and those starred are believed to be Auger peaks arising from excitation by the plasma electrons from the lamp and/or NeII radiation. In both spectra, the peaks marked I arise from elastically scattered electrons. (XBL 763-2444A)

Fig. 2. Photoelectron spectra of Sm^+ . (a) Excited by HeI lines. The vertical bars are the estimated positions and intensities of the $6H$, $6F$, and $6P$ terms of the $(4f^5 6s^2)$ configuration (see text). (b) Excited by NeI line. The nature of the band at 10.5 eV is not known. (XBL 767-3238A)

Fig. 3. Photoelectron spectra of Eu^+ . (a) Excited by HeI lines. The lines marked S_β and S_γ are due to ionization by HeI β and HeI γ lines. (b) Excited by NeI line. In both spectra, the lines marked I are elastically scattered electrons. (XBL 7512-9596A)

Fig. 4. Photoelectron spectra of Yb^+ . (a) Excited by HeI lines. The lines marked S are due to ionization by HeI β line. (b) Excited by NeI line. In both spectra, the lines marked I are elastically scattered electrons. (XBL 761-2030A)

Table 1. Observed states of Ba^+ and relative peak intensities in HeI and NeI spectra.

Ba^+ state ^a	Binding ^b energy (eV)	Optical ^c value (eV)	Intensity ^d HeI	Intensity ^e NeI
6s $^2\text{S}_{1/2}$	5.211	5.211	100; 0.6	100; 1.6; 5.4; 0.8
5d $^2\text{D}_{3/2}$	5.81	5.816	72; 0.9	{ 22; 2.2; 5.0; ---
$^2\text{D}_{5/2}$	5.91	5.915	160; 0.8	
6p $^2\text{P}_{1/2}$	7.72	7.723	36	1.5
$^2\text{D}_{3/2}$	7.93	7.933	63	3.2
7s $^2\text{S}_{1/2}$	10.46	10.463	38	0.7
6d $^2\text{D}_{5/2,3/2}$	10.92	10.908; 10.934	108	0.7
4f $^2\text{F}_{7/2,5/2}$	11.20	11.195; 11.222	19	0.5
7p $^2\text{P}_{1/2}$	11.33	11.335	15	
$^2\text{P}_{3/2}$	11.40	11.412	33	
5f $^2\text{F}_{5/2,3/2}$	12.34	12.327; 12.357	28	
8s $^2\text{S}_{1/2}$	12.40	12.405	47	
7d $^2\text{D}_{5/2,3/2}$	12.63	12.626; 12.637	37	
8p $^2\text{P}_{3/2,1/2}$	12.84	12.816; 12.853	20	
5g $^2\text{G}_{9/2,7/2}$	13.02	13.026	11	
6f $^2\text{F}_{7/2,5/2}$	13.22	13.220; 13.233	10	
9s $^2\text{S}_{1/2}$	13.35	13.355	5	
8d $^2\text{D}_{5/2,3/2}$	13.48	13.478; 13.484	7	
9p $^2\text{P}_{3/2,1/2}$	13.61	(13.583; 13.603)	12	
6g $^2\text{G}_{9/2,7/2}$	13.69	13.695	13	
7f $^2\text{F}_{7/2,5/2}$	13.79	13.792; 13.798	3	
10s $^2\text{S}_{1/2}$	13.89	13.892	2	
9d $^2\text{D}_{5/2,3/2}$	13.96	13.967; 13.971	2	
10p $^2\text{P}_{3/2,1/2}$	14.04	(14.031; 14.045)	4	
7g $^2\text{G}_{9/2,7/2}$	14.10	14.099	5	
(11s) 10	14.22	(14.226)	0.65	
(11p) 9	14.32	(14.317; 14.325)	0.40	
(12s) 8	14.45	(14.447)	0.28	
7	14.56		13	
6	14.66		2	
5	14.77		3	
4	15.12		44	
3	15.28	15.283	291	
2	15.37	15.366	221	
1	15.42	15.420	81	

(Continued - Table 1.)

^aThe [Xe] core has been suppressed in this notation. Peaks 1-3 are Auger transitions. For other numbered states, the assignment is not final; see text.

^bThe error limit is less than 10 MeV.

^cOptical binding energies were obtained from Ref. 9a. The values in parentheses are binding energies estimated from the Rydberg formula, and those for states 1-3 are from Ref. 7.

^dIntensities are corrected for $\Delta E/E$ dependence and referenced to the Ba^+6s/HeI_{α} line. Where there are two entries, the first is from the HeI_{α} and the second from the HeI_{β} spectrum.

^eIntensities are corrected for $\Delta E/E$ dependence and referenced to Ba^+6s/NeI line. Where there is more than one entry, the first value is from NeI main line, and the others are from NeI S_3 , S_2 , and S_1 satellite lines.

Table 2. Observed states of Sm^+ and relative peak intensities in HeI and NeI spectra.

Sm^+ state ^a	Binding ^b energy (eV)	Optical value (eV)	Intensity ^e HeI	Intensity ^e NeI
$4f^6 6s \begin{smallmatrix} 8F \\ 6F \end{smallmatrix}$	5.64 (2)	5.63 ^c	27	100
	5.80 (2)	5.82 ^c	100	100
$4f^6 5d$	6.61 (2)	6.52-8.19 ^c	7	4
	6.94 (2)		18	4
	7.39 (2)		8	---
	7.70 (2)		8	---
	7.90 (2)		13	---
$4f^6 6p$	8.4 (1)	>8.27 ^c	20	<10
$4f^5 6s \begin{cases} 6H \\ 6F \\ 6P \end{cases}$	8.8 (1)	9.0 ^d	76	140
	9.6 (1)	9.7 ^d	35	77
	11.9 (1)	11.7 ^d	39	64

^aThe [Xe] core has been suppressed. The particular states of the $(4f^6 5d)$ and $(4f^6 6p)$ configurations cannot be identified, nor are the J values for all the states.

^bThe error is listed in parentheses. The binding energies for broad bands are the vertical values.

^cFrom Ref. 9b. The values for $6F$ and $8F$ correspond to the transitions $Sm(^7F_0) \rightarrow Sm^+(^8F_{1/2})$ and $Sm^+(^6F_{1/2})$ respectively.

^dThe values were estimated from Refs. 10 and 11 (cf. text), and are the weighted centers of the individual terms. Reference 10 gave $6H_{5/2}$ at (8.61 ± 0.25) eV.

^eThe intensities are corrected for the $\Delta E/E$ dependence of this type of spectrometer.

Table 3. Observed states of Eu^+ and relative peak intensities in HeI and NeI spectra.

Eu^+ state ^a	Binding ^b energy (eV)	Optical ^c value (eV)	Intensity ^d HeI	Intensity ^d NeI
$4f^7 6s \ ^9S_4$	5.67	5.670	52; 4.5; 1.9	95
$\quad \quad \quad ^7S_3$	5.88	5.877	100; 8.1; 1.5	100
$4f^7 5d \ ^9D_{2,3,4,5,6}$	6.96	6.900-7.049	26; 9.8; 0.7	12
$\quad \quad \quad ^7D_{1,2,3,4,5}$	7.77	7.760-7.817	32	10
$4f^7 6p \ ^9P_{3,4}$	8.67(5)	8.617; 8.670	3	7
$\quad \quad \quad ^9P_5$	8.92	8.914	0.6	2
$\quad \quad \quad ^9P_{4,3,2}$	9.04	8.997; 9.029; 9.048	2	4
$4f^6 6s^2 \ ^7F_0$	9.99(3)	---	114	226
$\quad \quad \quad ^7F_1$	10.07	---		
$\quad \quad \quad ^7F_2$	10.15	---		
$\quad \quad \quad ^7F_3$	10.25	---		
$\quad \quad \quad ^7F_4$	10.37	---		
$\quad \quad \quad ^7F_5$	10.46	---		
$\quad \quad \quad ^7F_6$	10.55	---		
$4f^7 7s \ ^9S_4; ^7S_3$	11.79(3)	11.761; 11.825	2	---
$4f^7 6d \ ^9D; ^7D$	12.42	12.399-12.438	1	---

^aThe [Xe] core has been suppressed.

^bThe error limit is 20 MeV except as listed in parentheses. The binding energies for broad bands are the vertical ones.

^cFrom Ref. 9c.

^dThe intensities are corrected for the $\Delta E/E$ dependence and referenced to the 7S_3 line. Where there are three entries in the HeI column, they are from HeI α , HeI β , and HeI γ spectra respectively.

Sm/NeI (730°C), Eu/HeI (740°C), Eu/NeI (740°C), Yb/HeI (650°C), and Yb/NeI (600°C).

By analogy to the Group II elements,³ the ground states of the lanthanides can be approximated by ISCI as

$$\Psi = a|6s^2; ^1S> + b|5d^2; ^1S> + c|6p^2; ^1S> + \dots, \quad (1)$$

when the [Xe] core and the 4f-electrons have been suppressed, and $a \gg b \sim c$. Consequently, the photoelectron spectra of Ba and the lanthanides will show, in addition to intense peaks due to the 6s ionic states, weak lines corresponding to states such as 5d, 6p, etc. This is indeed the case with the

NeI spectra of these atoms (see Figs. 1-4b), and the HeI spectrum of Yb (see Fig. 4a). Therefore, we have assigned the satellites in these cases to ISCI.

The intensities of the ISCI satellites depend upon the CI coefficients a, b, c , etc. in Eq. (1) as well as the differential photoionization cross sections. The latter normally vary smoothly with photon energy, barring the existence of Cooper minimum and resonance, and over a small span of energy, say 5 - 10 eV, an order of magnitude change in cross sections is not expected. Consequently, if the satellites are interpreted entirely in terms of ISCI, the shapes of the spectra excited by HeI (21.22 eV) and NeI (16.9 eV) radiation should reveal little difference. This was indeed observed in Ca and Sr.³

Table 4. Observed states of Yb⁺ and relative peak intensities in HeI and NeI spectra.

Yb state ^a	Binding ^b energy (eV)	Optical ^c value (eV)	Intensity ^d HeI	Intensity ^d NeI
4f ¹⁴ 6s 2S _{1/2}	6.25	6.254	100	100
4f ¹⁴ 5d 2D _{5/2}	9.2	9.271	6	10
4f ¹³ 6s ² 2F _{7/2}	8.91	8.910	180	281
2F _{5/2}	10.17	10.168	95	135
4f ¹⁴ 6p 2P _{1/2}	9.61	9.609	3	3
2P _{3/2}	10.02	10.022	5	5
----	9.82		2	6
----	11.77		7	2
----	12.37		8	9
----	13.53		11	12
----	14.68		4	---

^aThe [Xe] core has been suppressed. Some states have not been identified.

^bThe error limit is 20 meV.

^cThe binding energies are from Ref. 9d.

^dThe intensities are corrected for ΔE/E dependence and referenced to the Yb⁺6s line.

Among the cases studied here, the spectra of Yb fall within the above expectation while those of Ba, Sm, and Eu showed differences too large to be explained in terms of ISCI alone. The unexpected features all appeared at the photon energies of HeI radiation (for Ba, at more energetic NeI lines as well) and can be summarized as follows. (1) The relative intensities of the satellites are far too large to be expected from ISCI considerations. This behavior is dramatized in the HeI spectrum of Ba (Fig. 1a) which showed a number of satellites with intensities comparable to the 6s main line. This trend is further continued at several photon energies close to the HeIα (21.22 eV) line. (2) The intensity ratios of the exchange multiplets of Sm⁺(4f⁶6s; ^{6,8}F) (Table 2) and Eu⁺(4f⁷6s; ^{7,9}S) (Table 3) deviate considerably from their respective statistical multiplicity ratios.

The remarkable contrast between the HeI and NeI spectra of Ba, together with the evidence from absorption⁵ and previous photoemission work,^{6,7} firmly establishes that autoionization processes are occurring in the HeIα spectrum. The HeIα line overlaps a 5p absorption line such that a Rydberg state is resonantly excited. This state is mixed, through CI, with a number of continuum states such as

$$[(Ba^+ 5p^6 n\ell)(\epsilon\ell')]_{J=1}^0, [(Ba^+ 5p^5 n\ell n'\ell')(\epsilon\ell'')]_{J=1}^0,$$

and

$$[(Ba^{++} 5p^6)(\epsilon\ell')(\epsilon\ell'')]_{J=1}^0 \cdot \text{Resonant excitation and autoionization}$$

of this state thus gives rise to the various peculiar features observed in the HeI spectrum. This

process is described schematically in Fig. 5. The admixed $(Ba^+ 5p^6 n\ell)(\epsilon\ell')$ states autoionize directly to yield the $Ba^+(5p^6 n\ell)$ lines, which are detected as peaks through the kinetic energies of the continuum electrons. $(Ba^{++} 5p^6)(\epsilon\ell)(\epsilon\ell')$ decays to the $Ba^{++}(5p^6)$ state by giving off two continuum electrons, yielding a continuous electron distribution at energies above the Ba^{++} threshold (15.215 eV). The $(Ba^+ 5p^5 n\ell n'\ell')(\epsilon\ell'')$ manifold first autoionizes to form the highly-excited $(Ba^+ 5p^5 n\ell n'\ell')$ states, yielding the three peaks at very low kinetic energies; i.e., at ca. 0.1 eV, detected by Hotop and Mahr.⁷ These resulting Ba^+ states can undergo further Auger transitions to the $Ba^{++}(5p^6)$ state, with the corresponding Auger electrons detected at ca. 5.9 eV (peaks 1, 2, and 3 in Fig. 1a).

The photoelectron lines (labeled S in Fig. 1a) excited by HeIβ radiation again shows two unusual features that indicate the occurrence of autoionization. First, the 5d/6s intensity ratio is ~3/1 which is not expected from the ISCI model. Next, the 5d_{5/2}/5d_{3/2} ratio is ~1/1.1, as opposed to the multiplicity ratio 3/2. It is worthwhile noting that the multiplicity ratios are observed rather well in the HeI spectrum (cf. Table 1). As suggested by Brehm and Höfler,⁶ the peaks 4-10 in Fig. 1a may be assigned to the higher Rydberg states converging to the Ba^{++} threshold. If this is the case, the sudden increase in the intensities of these lines seems unexpected judging from the trend of other satellite intensities. In view of our finding that autoionization occurs at the HeIβ line energy, it is likely that part of the electron intensity between peaks 4 to 10 arises in the same way as do peaks 1 to 3, i.e., via a two-step autoionization-

Table 5. The energies and relative line intensities of the HeI and NeI resonance radiation spectra.

Source	Excited state	Designation	Wavelength (Å) ^a	Energy (eV)	Relative intensity ^b
Helium capillary discharge	2^1P_1	HeI α	584.334	21.2175	100
	3^1P_1	HeI β	537.030	23.0864	4.5(1.0)
	4^1P_1	HeI γ	522.213	23.7415	0.6(0.2)
Neon capillary discharge	$3s [3/2]_1^o$	NeI	743.718	16.6704	27(5)
	$3s'[1/2]_1^o$	doublet	735.895	16.8476	100
	$4s [3/2]_1^o$	S_3	629.74	19.688	0.5(0.2)
	$4s'[1/2]_1^o$		626.82	19.779	
	$3d [1/2]_1^o$	S_2	619.10	20.026	0.2(0.1)
	$3d [3/2]_1^o$		618.67	20.040	
	$3d'[3/2]_1^o$		615.63	20.139	
	$5s [3/2]_1^o$	S_1	602.73	20.570	0.1(0.1)
	$5s'[1/2]_1^o$		600.01	20.663	
	$4d [1/2]_1^o$		598.88	20.702	
	$4d [3/2]_1^o$		598.68	20.709	
	$4d'[3/2]_1^o$		595.92	20.805	
	$6s [3/2]_1^o$	S_0	591.82	20.949	0.03(0.03)
	$6s'[3/2]_1^o$		589.18	21.043	
	$5d [1/2]_1^o$		590.02	21.013	
	$5d [3/2]_1^o$		589.91	21.017	
	$5d'[3/2]_1^o$		587.23	21.113	

^aReference 9a.^bThe relative intensity was determined by the Xe $2P$ doublet. The values in parentheses are the probable errors, predominantly due to intensity fluctuations in the source.

Auger process. Unfortunately, the corresponding autoionizing electrons were not detected due to poor analyzer transmission at low energies; otherwise the above assignment could be tested.

Autoionization also appears to occur at the various NeI line energies as peaks S_1, S_2, S_3 in Table 5 and Fig. 1b. This is suggested by the high photoelectron line intensities relative to the relative radiation line intensities in the usual photon flux from NeI sources, as well as the large intensity ratio of the 5d to 6s states. Furthermore, these NeI lines lie right at the seemingly continuous absorption region of the Ba absorption spectrum.⁵ The autoionizing states involved at the NeI line energies do not seem to undergo a two-step ionization, as there is no indication for the existence of the corresponding electron lines in the spectrum (Fig. 1b).

Following the analysis of the photoelectron spectra of Ba, the differences between the HeI and NeI spectra of Sm and Eu can be understood also in terms of autoionization processes. Therefore, autoionization is suggested by the spectra to occur at the HeI α line energy for Sm, and at HeI α and HeI β energies for Eu. For all three cases, the intensity ratios measured from spectra of the multiplets of the ground ionic states deviate considerably from the expected statistical ratio (see Figs. 2b and 3b). Intuitively, this large deviation is quite unexpected, considering the similarity of the states involved, but it appears to reflect the subtlety of the interaction in the final states. For Yb, the $(5p)^{-1}$ threshold is high enough in energy so that no autoionizing levels are accessible by either NeI or HeI radiation.⁸ Thus, the spectrum and intensities (Table 4) observed in Yb may be adequately described in terms of ISCI alone. One is therefore

Fig. 5. Energy illustrating the autoionization process of Ba at HeI energy. The 5p thresholds are from this work and the energy of $(5p^5 6s 5d)$ is from Ref. 7. All other energy levels are from C. E. Moore, NBS Circ. 467, Vol. 3 (1962). (XBL 761-2034B)

led to conclude that the contribution of autoionization to the HeI spectra of the lanthanides that was first observed in Ba has ended by Yb.

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15. GLOW DISCHARGE LAMPS AS ELECTRON SOURCES FOR ELECTRON IMPACT EXCITATION

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It is well-known that the plasma of any gas discharge provides a copious source of electrons. The energy of the electrons in the plasma follows a Maxwellian distribution,¹ with a mean energy rarely exceeding one-third of the first ionization potential of the gas involved. We have found it possible to utilize the plasma in the discharge lamp of a conventional ultraviolet photoelectron spectrometer as an electron source for low energy electron impact excitation.

Ejected electron spectroscopy following electron impact detects electrons of discrete energies and, as a consequence, the monochromatic electrons can easily be distinguished from the abundant continuous background. Electrons ejected from autoionizing states or Auger transitions satisfy this condition, and can therefore be detected and studied with broad-band electron sources. In addition, low energy electron impact excitation is not governed strictly by optical selection rules, thus, "forbidden" transitions may be observed.

The experiments were carried out on a Perkin Elmer PS-18 photoelectron spectrometer modified for high temperature work.^{3,4} Except for the operation of the discharge lamp, the spectrometer was used in exactly the same manner as for the measurement of photoelectron spectra.

The PS-18 spectrometer uses a dc high-voltage cold cathode capillary discharge for generating HeI or other atomic resonance radiation. The cross-sectional view of the lamp is shown in Fig. 1. The upper and of the capillary in the lamp is about 10

Fig. 1. Schematic diagram of the discharge lamp.
(XBL 764-2762)

cm below the entrance slit of the 127° cylindrical electron analyzer. When the lamp is operated to produce HeI radiation, a pressure of 200-500 microns is used. In this pressure range electrons from the discharge plasma cannot reach the entrance slit because of inelastic collisions. Maintaining this condition is mandatory in PES work, because electrons from the lamp can increase the noise level and lower the quality of the photoelectron spectra. In contrast, to operate the lamp as an electron gun, the plasma was intentionally diluted to increase the mean free path of the electrons and enable them to enter the ionization chamber. This was accomplished by lowering the pressure in the discharge while monitoring the background electron counts. By adjusting the pressure, an optimum condition for signal-to-background ratio, signal intensity and resolution in the ejected electron spectrum can usually be obtained. Depending upon the cleanliness and exact geometry of the lamp and the sample used, the helium lamp was found to operate as an electron gun in the pressure range of 25-150 microns, with a discharge current of ca. 50 mA.

To illustrate the performance of the cold cathode plasma, the N_{4500} Auger spectrum of Xe recorded using five different plasma discharges is shown in Fig. 2. Included for comparison is the corresponding spectra reported by Werme, et al.,⁵ who used a filament electron gun. Among the five lamps tested, (He, Ne, Ar, H₂, N₂), the helium lamp was consistently more stable and it gave spectra of better signal-to-background ratio.

Comparison of our results with the spectra obtained by Werme, et al.⁵ (Fig. 2) shows that they are almost identical in the positions and relative intensities of the Auger peaks. Furthermore, the strong autoionization electron peaks lying between 8-10 eV in the Xe spectrum of Werme, et al. also

Fig. 2. The N_{4500} Auger spectra of Xe excited by electrons produced from hot filaments (a) and the plasmas of different discharge lamps as indicated (b) - (f).
(XBL 7512-9905)

are present in all the spectra obtained by plasma electrons. Naturally, the spectra obtained by a normal electron gun are much superior in signal-to-background ratio. The higher background in our spectra is mainly due to poor focusing of the electron plasma and immense scattering of electrons from the ionization chamber. The signals are much stronger in the electron plasma spectra which was partially achieved at the expense of resolution. In addition, besides being inexpensive and convenient, the plasma source may be used to study reactive substances, which might "poison" a conventional electron gun.

Figure 3 depicts the autoionization electron spectrum of K vapor at $220 \pm 20^\circ\text{C}$. The spectrum corresponds to the autoionizing states of K with a 3p-electron excited by electron impact. Similar spectra have been reported recently² using electron

Fig. 3. The autoionization electron spectrum of K vapor. (XBL 763-2477A)

beams of energy 500 and 29 eV. Most of the states detected in the electron spectra have also been observed in the 3p absorption spectrum of K.⁶ Peaks 4-8 are observed only upon low energy electron impact excitation and must be regarded as optically forbidden transitions.^{2,6} The broad peak 1 has not been reported before, but appeared to be present in Fig. 1 of Ref. 2. We have found the intensity of this peak to increase the temperature of the oven, and thus it is tentatively assigned to potassium dimer, K₂. With the binding energy of K₂ at 4.0 eV,⁷ the excitation energy of this autoionizing state is 17.9 eV. The peaks labeled by I are the inelastic loss peaks of lines 2 and 3 corresponding to 4s → 4p excitation in K.

Figure 4 shows the autoionizing electron spectrum of Na vapor at 270±20°C. Core-excited autoionizing states in Na have been observed by photoabsorption^{8,9} and projectile-electron spectroscopy.¹⁰ Except for peaks 1, 2, and 5, the spectrum of Na corresponds to the autoionizing states of Na following the excitation of a 2p electron. Peaks 3 and 4 are associated with the spin-orbit (s-o) doublets of the 2p³s² state of Na. The peaks between 28 and 30 eV are optically forbidden states of configuration 2p⁵3s3p, observed previously only in Na⁺-He collisions.¹⁰

The electron intensity around peaks 1 and 2 is due to L₁L₂3M₁ Coster-Kronig transitions, i.e., Na⁺(2s2p⁶3s; 1,3S) → Na⁺⁺(2s²2p⁵; ²P_{1/2,3/2}) + e. The electron intensity around peak 5 cannot be satisfactorily attributed to autoionizing states with the excitation of a 2p-electron. It is tentatively assigned to the L₁L₂3N₁ Coster-Kronig transition, i.e., Na⁺(2s2p⁶4s; 1,3S) → Na⁺⁺(2s²2p⁵; ²P_{1/2,3/2}) + e.

In light of these results, one should be cautious about the presence of autoionizing electron lines in the photoelectron spectra, especially of those compounds containing heavy elements, when recorded in a Perkin-Elmer spectrometer. It seems worthwhile pointing out that in the photoelectron spectra of Ca and Sr, autoionizing electrons have been detected with appreciable intensities with the He lamp operating at a pressure as high as 200 micron. On the other hand, it should prove very

Fig. 4. The autoionization electron spectrum of Na vapor. (XBL 763-2475)

useful to study autoionization spectra in UV spectrometers simply by lowering the pressure.

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16. ELECTRON IMPACT EXCITATION OF ELECTRON CORRELATION STATES IN Ca, Sr, AND Ba

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By taking advantage of the recently developed electron impact excitation capabilities of our Perkin-Elmer PS-18 photoelectron spectrometer,¹ we have recorded the low energy autoionization electron spectra of Ca, Sr, and Ba. The spectra were obtained under the same conditions as the high temperature photoemission² work and are displayed in Fig. 1.

The peaks corresponding to the M⁺(ns²(n+1)p⁵) ²P_{3/2} and ²P_{1/2} states are: 13 and 14 for Ca⁺; 4

Fig. 1. Autoionization electron spectrum of Ca, Sr, and Ba. (XBL 763-2476B)

and 5 for Sr^+ ; 14 or 15 and 22 for Ba^+ . Besides these intense primary lines, there are in the spectrum a number of "satellites" with comparable intensities. Unambiguous assignments for these lines are difficult, due to the continuous nature of our source, and the less stringent selection rules for low energy electron impact excitation. A qualitative discussion of the origins of these peaks follows. It is interesting to note however, that the three intense peaks associated with double autoionization in the HeI photoelectron spectrum of $\text{Ba}^{3,4}$ corresponding to peaks, 1, 2, and 3 in Fig. 1 (Ba), have relatively small intensities in the electron spectrum.

Following the electron impact excitation of one of the outermost core-like electrons in Ca, Sr, or Ba, there are three possible ways to produce ejected electrons with discrete energies. They are designated e_1 , e_2 , and e_3 in Fig. 2 and correspond to the following autoionization processes:

$$M^*(np^5 n' l' n'' l' n''' l''') \rightarrow M^+(np^6 (n+1)s \text{ or } np^6 n' l') + e_1$$

$$M^*(np^5 n' l' n'' l' n''' l''') \rightarrow M^{*+}(np^5 n' l' n'' l'') + e_2$$

$$M^*(np^5 n' l' n'' l'') \rightarrow M^{++}(np^6; {}^1S_0) + e_3,$$

where $n=3, 4$, and 5 for Ca, Sr, and Ba respectively. Electrons e_1 , e_2 , and e_3 lie in different

Fig. 2. Autoionization in M; M=Ca, Sr, or Ba. (XBL 763-2554)

energy regions, and as such, they can usually be distinguished from one another. Generally speaking, e_2 -type electrons are of extremely low energy, and the centers of the electron groups e_1 and e_3 are separated by the binding energy of M^+ . From simple estimates of energies, we have found that the e_3 electrons must contribute predominantly to the observed electron spectra of Ca, Sr, and Ba.

There are two ways by which $M^{*+}(np^5 n' l' n'' l'')$ states can be populated (Fig. 2), i.e., via excitation (A) and subsequent autoionization (e_2) or by direct ionization (B). If process B is the major contributor to M^{*+} states, the resulting electron spectrum should be dominated by the s-o doublets of $M^{*+}(np^5 (n+1)s^2; {}^2P_{1/2, 3/2})$, with the "satellite" states appearing in small intensities. This is certainly not the situation especially in Ba (Fig. 1). In contrast, the observed spectrum is expected if Ba^{*+} states are reached predominantly through excitation and subsequent autoionization. Consequently, the s-o $5p^{-1}$ partners are not observed in statistical ratio in Ba, and a large number of satellites with appreciable intensities are present. Similar arguments and conclusion also apply to Ca and Sr.

The reason that autoionization rather than direct ionization is mainly responsible for the population of M^{*+} states is due to the collapse (or near degeneracy) of the nd into the $(n+1)s$ shell as a result of np excitation or ionization. We note, however, the corresponding arguments do not apply to Mg, where 3s and 3d shells are involved, and consequently autoionization e_2 is not readily allowed on energy grounds. Therefore, the low energy electron spectrum of Mg^5 is dominated by the $2p^5 3s^2$ autoionizing states as expected from direct ionization (B).

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17. PHOTOELECTRON SPECTROSCOPY OF ATOMIC AND MOLECULAR BISMUTH

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The HeI photoelectron spectra¹ of Bi and Bi₂ were recorded by studying bismuth vapor at (750±20) °C. The spectra are shown in Fig. 1 and the parameters derived from it are collected in Table 1. As-

signments of atomic peaks were made by comparison of binding energies with optical data. Some of the molecular lines of Bi₂ are easily distinguishable by their larger widths. Additional identification was accomplished by noting the behavior of the line intensities with respect to the oven temperature. The intensities of the group of lines belonging to Bi₂ decreased with increasing temperature relative to that of atomic peaks, while the relative intensities with each group remained unchanged.

Table 1. Observed states of Bi⁺ and Bi₂⁺.

Ion	Final State		Apparent Relative Intensity	Experimental FWHM(a) (eV)	Vertical Binding Energy(a) (eV)	Apparent Adiabatic Binding Energy(b) (eV)	Energy from Other Data (eV)	
Bi ⁺	6s ² 6p ²	³ p ₀	100	0.075	7.29(3)		7.289 ^(c)	
		³ p ₁	320(50)	0.08	8.94(3)		8.942	
		³ p ₂	510(40)	0.08	9.40(3)		9.401	
	6s ² 6p ²	¹ d ₂	16(3)	0.07	11.49(3)		11.495	
	6s6p ³	⁵ s ₂	26(5)	0.07	16.73(3)		16.730	
	6s ² 6p _{1/2} 6d _{3/2}	³ d ₂	54(10)	0.08	17.12(4)		17.090	
		³ d ₁		—	—		17.274	
	6s ² 6p _{1/2} 6d _{5/2}	³ f ₂	54(10)	0.07	17.47(4)		17.457	
		³ f ₃		—	—		17.483	
	Bi ₂ ⁺	(σ _u 6s) ² (σ _g 6p) ² (π _u 6p) ³		² Π _{u,3/2}	220(20)	0.27	7.53(3)	7.35(5)
² Π _{u,1/2}				340(50)	0.26	8.94(5)	8.65(5)	8.9
(σ _u 6s) ² (σ _g 6p)(π _u 6p) ⁴		² Σ _g ⁺	240(30)	0.09	9.30(3)	9.30(3)	—	
(σ _u 6s)(σ _g 6p) ² (π _u 6p) ⁴		² Σ _u ⁺	4(2)	0.07	14.87(3)	14.87(3)	—	

- a) This work, with areas corrected for ΔE/E = Constant, with intensities given relative to ³P₀, taken as 100. Xe and Ar were used for calibration. Experimental errors are given parenthetically.
b) No correction for thermal population of vibrational levels in the ground state have been employed.
c) Optical data from Ref. 3.
d) Electron impact data from Ref. 2.

The spectrum of Bi was found consistent with a j-j coupling description of the ground state. $^3P_{0,1,2}$ and 5S states are due to ionization of one of the 6p and 6s electrons respectively. Satellite peaks 1D_2 at 11.49 eV, and $^3D_{1,2}$ at 17.12 eV and $^3F_{2,3}$ at 17.47 eV were also observed. They were assigned to admixtures of the configurations

$[(6s_{1/2})^2 6p_{1/2}(6p_{3/2})^2]_{3/2}$ and $[6s^2 6p 6d^2]_{3/2}$ into the main ground state configuration $[(6s_{1/2})^2 (6p_{1/2})^2 (6p_{3/2})^2]_{3/2}$. An autoionization process at the energy of HeI γ radiation (23.74 eV) was suggested by the large intensity of the HeI γ spectrum and the nonstatistical intensity ratio of the $^3P_{0,1,2}$ states, which can be seen in Fig. 2 and Table 2.

Fig. 1. The HeI photoelectron spectrum of atomic and diatomic bismuth.
(XBL 762-2301)

Table 2. Relative intensities^a of 3P_0 , 3P_1 , and 3P_2 with different HeI lines.

Ion State	HeI α (21.22 eV)	HeI β (23.09 eV)	HeI γ ^c (23.74 eV)	
3P_0	100	3.0 (.5)	6.7 (1)	[1.0]
3P_1	320 (50)	~ 2 (1)	7.3 (1)	[1.1 (.1)]
3P_2	510 (40)	b —	7.9 (1)	[1.2 (.1)]

a) Areas corrected for $\Delta E/E = \text{constant}$ and normalized to 3P_0 (HeI α).

b) This peak is overlapped by the $^2\Pi_{u,3/2}$ line of Bi_2^+ ; thus no estimate is possible.

c) Values in square brackets are normalized to 3P_0 .

Fig. 2. The expanded portion of Fig. 1 from 6 to 11 eV, showing the molecular lines of Bi_2 .
(XBL 761-2031)

The photoelectron spectrum of Bi_2 showed three distinguishable bands at 7.53 eV, 8.94 eV, and 9.30 eV corresponding respectively to the ionic states $^2\Pi_{u,3/2}$, $^2\Pi_{u,1/2}$, and $^2\Sigma_g^+$ due to ionization of a (π_{u6p}) or (σ_{g6p}) electron. A probable fourth band was observed at 14.87 eV, and was tentatively assigned to $^2\Sigma_u^+$ of Bi_2^+ formed from (σ_{u6s}) ionization. The spectrum of Bi_2 was found similar to those of lighter Group VA diatomics. By comparison with other Group VA diatomics, a linear relationship between the equilibrium internuclear distance and the difference between the binding energies of (σ_{g6p}) and (π_{u6p}) MO's was found, and is shown in Fig. 3.

Fig. 3. The plot of internuclear distances (r_e) vs. the differences in the binding energies ($\Delta E_{B.E.}$) of the two lowest occupied MO's $\sigma_g(p)$ and $\pi_u(p)$.
(XBL 762-2302)

This trend reflects the increased bonding effectiveness of (σ_{np}) MO as the nuclei move further from the center of the charge overlap.⁴

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18. RELATIVISTIC EFFECTS IN THE UV PHOTOELECTRON SPECTRA OF GROUP VI DIATOMIC MOLECULES

S.-T. Lee, * Ş. Süzer,† and D. A. Shirley

The HeI photoelectron spectra of the homonuclear dichalcogens¹ have shown the intensity ratio of $^2\Pi_{g,1/2}/^2\Pi_{g,3/2}$ to be increasingly larger than 1, the statistical ratio, with increasing molecular weight (Table 1). We² have shown this phenomenon to arise from spin-orbit (s-o) coupling in the ground state. As the s-o coupling gets stronger, it becomes more appropriate to describe the coupling of angular momenta in heavier dichalcogens in Hund's case c rather than case b coupling. If only the electronic states are considered, this is equivalent to using ω - ω coupling rather than Λ - Σ coupling, the molecular equivalents of j-j and L-S couplings respectively for atoms. In ω - ω coupling, the s-o interaction splits the π MO into $\omega=1/2$ and $3/2$ orbitals, the former being lower in energy. For Group VI diatomics, the ground state of π^2 configuration can then be approximated by a simple configuration-interaction expansion

$$\Psi(XO_g^+) = a(1/2, 1/2)_0 + b(3/2, 3/2)_0. \quad (1)$$

In this picture, the intensity ratio $^2\Pi_{g,1/2}/^2\Pi_{g,3/2}$ is to first approximation given by a^2/b^2 . The relative weights of a and b depend on the strength of s-o interaction. In the absence of s-o coupling, the ground state is

$$\Psi^o(X^3 \sum_{g,0}^- \text{ or } XO_g^+) = \frac{1}{\sqrt{2}} (1/2, 1/2)_0 + \frac{1}{\sqrt{2}} (3/2, 3/2)_0. \quad (2)$$

and the $^2\Pi_{1/2}/^2\Pi_{3/2}$ ratio is 1. By contrast, if the s-o coupling is large, then the ground state will be predominantly $(1/2, 1/2)_0$ and the ratio $a^2/b^2 > 1$, or $X^2\Pi_{g,3/2}$ may hardly be detected at all. This is believed to be the explanation for the anomalous $^2\Pi_{1/2}/^2\Pi_{3/2}$ intensity ratios observed in the photoelectron spectra of S_2 , Se_2 , and Te_2 .

Table 1. Calculated and experimental branching ratios of ${}^2\Pi_{g,1/2}/{}^2\Pi_{g,3/2}$ of Group VI diatomics.

Molecule	$\zeta_{np}(\text{eV})^a$	K(eV)	$E(XO_g^+)(\text{eV})^b$	C_2/C_1	a^2/b^2	${}^2\Pi_{g,1/2}/{}^2\Pi_{g,3/2}^c$
O_2	0.0187	1.331	-1.31×10^{-4}	-7.02×10^{-3}	1.03	1.01
	0.0187	—	$-4.92 \times 10^{-4*}$	-2.63×10^{-2}	1.11	1.04
S_2	0.0474	0.855	-1.31×10^{-3}	-2.77×10^{-2}	1.12	1.04
	0.0474	—	$-2.94 \times 10^{-3*}$	-6.19×10^{-2}	1.28	1.10
Se_2	0.210	0.779	-2.78×10^{-2}	-0.132	1.70	1.38
	0.240	0.779	-3.61×10^{-2}	-0.151	1.84	1.43
	0.210	—	$-4.55 \times 10^{-2*}$	-0.216	2.41	1.74
	0.240	—	$-4.55 \times 10^{-2*}$	-0.190	2.16	1.61
Te_2	0.389	0.677	-0.104	-0.267	2.99	2.99
	0.530	0.677	-0.183	-0.345	4.21	4.21
	0.389	—	-0.276*	-0.711	35.0	35.0
	0.530	—	-0.276*	-0.521	10.1	10.1
Po_2^g	1.688	0.586	-1.20	-0.711	35.2	35.2

a) Atomic s-o coupling constants estimated from optical data (Ref. 9); for O_2 , S_2 , and the first ζ_{np} value of Se_2 and Te_2 , $\zeta_{np} = 2/3({}^3P_0 - {}^3P_2)$, while the second ζ_{np} value of Se_2 and Te_2 , and that for Po_2 were obtained from extrapolation using ζ_{np} values of their respective neighboring atoms in the Periodic Table as given in Ref. 10. These latter ζ_{np} 's were obtained in the intermediate coupling scheme, which are more appropriate for the heavier atoms.

b) The energy given here is referenced to the unperturbed $X^3\Sigma_g^-$. The E values are from calculation and those denoted by stars are the splittings $2\lambda_0$ in $X^3\Sigma_g^-$ given in Ref. 8.

c) First column are calculated ratios by weighting a^2/b^2 appropriately by accounting for the thermal population of l_g states, i.e., $l_g/0_g^+ = 2\exp[E(0_g^+)/kT]$, and second column are experimental results. No such correction is necessary for Te_2 and Po_2 .

d) Ref. 3 gives ~ 0.95 and Ref. 4 ~ 1.0 as estimated by present authors.

e) Estimated from Ref. 5 (Ref. 7 gives this estimated value as ~ 1.5).

f) Ref. 6 and 7.

g) The MO of Te_2 with principal quantum number of atomic functions raised correspondingly by 1 was used for Po_2 to calculate K.

In order to give more credence to this explanation, we have carried out an intermediate coupling calculation to estimate the ratio a^2/b^2 and compared it to the observed ${}^2\Pi_{1/2}/{}^2\Pi_{3/2}$ ratio. The calculation was done by expanding the ground state as

$$\Psi(X^3\Sigma_{g,0}^- \text{ or } XO_g^+) = C_1\Psi({}^3\Sigma_0^-) + C_2\Psi({}^1\Sigma_0^+). \quad (3)$$

With $\Psi({}^3\Sigma_0^-)$ given by Eq. (2) and

$$\Psi({}^1\Sigma_0^+) = -\frac{1}{\sqrt{2}}(1/2, 1/2)_0 + \frac{1}{\sqrt{2}}(3/2, 3/2)_0, \quad (4)$$

it can be shown² that $a/b = (C_1 - C_2)/(C_1 + C_2)$. Coefficients C_1 and C_2 were obtained through diagonalizing the matrix elements of the Hamiltonian that includes

electrostatic as well as s-o interactions. The results are collected in Table 1 and displayed pictorially in Fig. 1. In Table 1, K is the exchange

Fig. 1. Schematic correlation between A-Σ (extreme left), intermediate and ω - ω coupling (extreme right) showing the dependence of a^2/b^2 upon the relative strengths of $\mathbf{l} \cdot \mathbf{s}$ (ζ_{np}) and exchange (K) interactions. The coupling cases of the individual dichalcogens are indicated explicitly with electrons denoted by bars. (XBL 762-2337)

integral between the π MO's. In general, there is very good agreement between the calculated and experimental $2\pi_{g,1/2}/2\pi_{g,3/2}$ intensity ratios. It is worthwhile pointing out that the information in Fig. 1 can be applied to other cases as well as long as the relative strengths of s-o interaction and exchange integral is known.

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19. X-RAY PHOTOEMISSION SPECTRA OF THE 2s VALENCE ORBITALS IN CYCLIC ALKANES IN RELATION TO VALENCE BANDS OF AMORPHOUS GROUP IV AND V ELEMENTS

B. E. Mills* and D. A. Shirley

The valence-band x-ray photoelectron spectra of amorphous Ge, Si, As, Sb, and Bi display certain differences from the spectra of their crystals.^{1,2} One of the more striking differences is that two valence-band peaks in the cleaved crystal spectra are replaced by a broad peak in the amorphous case. These peaks all arise from bands built primarily from atomic s-like orbitals. The bands could differ in the crystalline and amorphous cases because of long-range disorder, short-range disorder, or a combination of both. We have studied model systems to help decide among these alternatives.

At standard conditions Ge and Si have the diamond structure. The atoms are tetrahedrally bonded to form connected chair-form six-membered rings. The group V elements have an A-7 crystal structure, also composed of six-membered rings. Radial distribution function measurements on the amorphous materials show little nearest-neighbor distance variation, but large variation in second-neighbor distance, suggesting a fixed bond length but variable bond angles. These features can in turn be met by a continuous random network model. An interesting structural feature of this model is that it can be constructed to have non-six membered rings. For example, Polk³ noted that there were 20% five-membered rings in his model. Another model, based on the ST-12 structure, would have 5, 6, 7 and 8-membered rings. It has been suggested that odd-membered rings could have a significant effect on the s-like valence band spectra of amorphous materials. This follows because these elements are covalently bonded, with localized orbitals. The s-levels, which are basically atomic, are sensitive to their local environment rather than to the crystal as a whole.

In order to definitively ascribe the change in valence-band spectra to ring size, one would like to be able to study covalent tetrahedral compounds of various ring sizes. Unfortunately, a crystal lattice of, for example, symmetrical interconnecting five-membered rings is impossible. However, a series of covalent tetrahedral molecules of every ring size exists—the cyclic alkanes. We have used these hydrocarbons as model compounds because of their availability and because of the cross section enhancement of the spectral region of interest in x-ray photoemission. Through the use of the cyclic alkanes we have confirmed the hypothesis that the s-like valence band spectrum reflects the local ring sizes in tetrahedrally-bonded solids.

Photoelectron spectra were taken on the 50 cm radius Berkeley magnetic spectrometer at a sample pressure of about 100 Torr. Cyclopentane, cyclohexane, cycloheptane, and cyclooctane spectra were taken with Mg K α x-rays at energy increments of 0.16 eV. To establish the value of cycloalkanes as model compounds for the solid structure in question, it now remains to show that cyclohexane is a good model compound for the s valence bands of diamond. Spectra of the valence bands of cyclohexane and diamond appear in Fig. 1, with the energy scale of

Fig. 1. A comparison of the XPS spectra of cyclohexane, diamond, and neopentane $[\text{C}(\text{CH}_3)_4]$. The energy axis of the diamond spectrum has been shifted to roughly align the peaks with those in cyclohexane. This procedure is necessary because gas and solid phase spectra are referenced differently and thus only energy differences can be compared accurately. (XBL 756-3127)

diamond shifted to correspond roughly with the cyclohexane spectrum. Also shown is the spectrum of $\text{C}(\text{CH}_3)_4$ (neopentane), to illustrate that simply having tetrahedral carbon bonds is not sufficient for simulating the diamond bands. If each data point in the cyclohexane spectrum is broadened by 0.8 eV (to reflect the interaction of the rings in the solid), the resulting spectrum shown at the top of Fig. 2, is almost identical to the diamond spectrum.

To understand the spectra of 2s orbital energies in the ring compounds, we have performed calculations at several levels of sophistication. We can use (and gain) the most physical insight at the simplest level, using the Hückel approximation in a qualitative way. At this level the eigenvalue problem for the σ orbitals describing C-C bonds is formally identical to that for the π system of planar cyclic aromatics, despite several obvious differences between the two problems. The earliest way to show this is to consider the problem of forming an N-membered ring of C-H moieties, by σ bonding, using a two-fold degenerate orbital on each. This leads with the usual approximations to a secular determinant with elements

$$D_{ij} = (\alpha - E) \delta_{ij} + \beta \delta_{i,j \pm 1}$$

Fig. 2. The spectrum of cyclohexane (see Fig. 1) broadened by 0.8 eV and spectra simulating different ring systems (also broadened by 0.8 eV). See text. (XBL 764-2760A)

where α and β are the usual Hückel integrals and the indices are taken modulo N (i.e., $D_{1N} = D_{N1} = \beta$) for $i, j = 1, 2, \dots, N$. The roots are

$$E_n = \alpha + \beta \cos \frac{2n\pi}{N}, \quad n = 0, 1, 2, \dots, N-1.$$

The eigenvalue spectra of these cyclic systems are well-known. For the present problem the important point is that a gap appears for the even rings that is filled by the odd rings.

To fit the molecular orbital spectra of these cyclic alkanes, not only the energies but also the wave functions must be accurately known. We found that extended Hückel theory gave excellent energies but unrealistic wavefunctions, and that two versions of CNDO theory gave neither satisfactory wavefunctions nor energies. The *ab initio* program GAUSS-70 gave very good energies and wavefunctions for C_5H_{10} , C_6H_{12} , C_7H_{14} , and C_8H_{16} .

Now that cyclohexane has been shown to be a good model for the s-like states of diamond, and assuming diamond to be a good model for the crystalline phases of interest, we can construct "spectra" for hypothetical tetrahedrally-bonded amorphous carbon according to different structural schemes and note the effect on the valence-band structure. To do

this we normalize the spectra of the ring compounds and then add the individual spectra together with weighting factors appropriate to the ring statistics of a given amorphous-lattice model. If we then broaden these "spectra" by 0.8 eV, we get something which can be directly compared to the "crystalline spectrum" in Fig. 2a.

Using Polk's model, for which he gave only the relative numbers of 5- and 6-membered rings, we get the "spectrum" in Fig. 2b. The minimum in the spectrum, which is still quite pronounced, is simply shifted toward lower binding energy. Indeed the dip merely shifts for any ratio of 5- to 6-membered rings. This can be seen in Fig. 2c, where we show the result of considering only these ring sizes in the ST-12 structure, which has twice as many 5- and 6-membered rings. The result is the same if only 6- and 7-membered rings are considered, except that in this case the minimum shifts to higher binding energy.

However, if we consider 5-, 6-, and 7-membered rings, which in ST-12 appear in the ratio 2:1:2, we get the curve shown in Fig. 2d. The two s-like peaks have not broadened significantly, nor has the splitting changed noticeably. The gap between them has simply been filled with new levels. To proceed one step further we can consider 8-membered rings. In ST-12 there are twice as many 8-membered rings as all the smaller ones combined. Including all these, one gets Fig. 2e. These 8-membered rings do not seem necessary to describe the spectra.

In conclusion, we have employed cyclic alkanes as model compounds to test the hypothesis that amorphous semiconductors possess topological disorder, yielding odd-membered rings and filling in the gap between the s-band peaks. Spectral synthesis showed that 5, 6, and 7-membered rings are necessary to explain the XPS spectra observed in amorphous materials. This strongly supports the topological disorder model. Of more general interest from the viewpoint of solid-state chemistry, this paper provides an example in which rather detailed molecular-orbital ideas are used to explain a fairly subtle point about the valence-band densities of states of covalent solids.

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20. RELATIVE GAS-PHASE ACIDITIES AND BASICITIES FROM A PROTON POTENTIAL MODEL

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The Bronsted acidity and basicity of a molecule, which measure that molecule's tendency to lose or

gain a proton, are of considerable chemical interest. The increasing availability of accurate experimental values of gas-phase acidities and basicities has stimulated interest in estimating these quantities theoretically. *Ab initio* calculations with sufficiently large basis sets can predict absolute values of the proton affinities to within a few per cent in the Hartree-Fock approximation. More accurate predictions of the absolute values of E_a and E_b would require very careful *ab initio* calculations, including electron correlations. Such calculations rapidly become impractical as the molecular size increases.

Relative acidities and basicities can be calculated to satisfactory accuracy using less sophisticated theoretical models. In this approach one tries to calculate the energy of the proton-transfer reaction

for comparing two bases, or

for comparing two acids. If the molecules to be compared lie in a group of molecules with enough similarities, some of the errors in E_b or E_a that arise from theoretical approximations will tend to cancel.

A potential model for this purpose was derived by Davis and Rabalais.¹ Based on differences in the electrostatic potentials at proton sites, calculated employing CNDO/2 wavefunctions, this approach is related to the "relaxation potential model" (RPM) used to estimate ESCA shifts. We shall term it the "proton potential model", or PPM. In this paper we report further results based on an improved PPM model.

In using the PPM approach to calculate the proton affinity of a reaction $M + H^+ \rightarrow MH^+$, the electrostatic potential at the proton site is evaluated from CNDO/2 wavefunctions calculated both with and without the proton present. Alternately we can describe these potentials as the values which would obtain if the proton had a charge of zero as well as +1, i.e., $V_N(0)$ and $V_N(1)$. Here N denotes proton attachment to a neutral molecule, and the V 's represent potential energies of +1 charges, rather than electrostatic potentials per se. It can be shown that the proton affinity is given to good approximation by

$$PA_N = -\frac{1}{2} [V_N(0) + V_N(1)] = -E_b.$$

Thus

$$E_b = V_N(1) + R_b.$$

Here $V_N(0)$ is the electrostatic potential energy at the proton site in the neutral molecule, and R_b is the relaxation or polarization energy at this site after the proton is added. For comparing two reactions to give

we would have

$$\Delta E_b(B_2-B_1) = E_{B_2} - E_{B_1} = PA_1 - PA_2 = \Delta V_N(0) + \Delta R_b,$$

where

$$\Delta V_N(0) = V_N^{B_2}(0) - V_N^{B_1}(0)$$

and

$$\Delta R_v = \frac{1}{2}[V_N^{B_2}(1) - V_N^{B_1}(1) - V_N^{B_2}(0) + V_N^{B_1}(0)].$$

When ΔV or ΔR is negative, the proton transfer reaction tends to proceed to the right, and vice versa. The $\Delta V_N(0)$ term represents an inductive effect in the usual chemical nomenclature, and is the heat of protonation in the (hypothetical) case of frozen, neutral-state molecular orbitals. The ΔR_b term corresponds to a polarization effect to adjust to the added proton. The separation and quantification of these two effects are useful features of the PPM approach.

In comparing the acidities of two molecules, we may relate the proton affinity of the anion to the energy of the ionization reaction

$$PA_a = -\frac{1}{2}[V_A(0) + V_A(1)] = E_a.$$

For the comparison of two acids we would have

$$\Delta E_a = -\Delta V_A(1) + \frac{1}{2} \Delta[V_A(1) - V_A(0)] = -\Delta V_A(1) + \Delta R_a.$$

Here $\Delta V_A(1)$ is the relative potential energy of the added proton in the neutral species, just as $\Delta V_B(0)$ was the relative potential energy at the protonation site in the neutral species for the protonation reaction. The terms ΔR_b and ΔR_a represent relative relaxation or polarization energies at the proton site in the positive or negative ion after the proton is gained or lost, respectively. For a given pair of molecules ΔR_b and ΔR_a are usually roughly equal in magnitude, according to the PPM calculations. For some classes of molecules it is possible to predict the relative sizes of $\Delta V_A(1)$ and $\Delta V_B(0)$, as well as those of ΔR_a and ΔR_b , from PPM calculations.

Table 1 lists values of ΔV and ΔR and derived values of ΔPA , calculated by the PPM method, for two groups of similar molecules for which experimental PA values are available. Good agreement with experiment was found for these two groups. For other groups the agreement was poorer, probably because of inadequacies in the CNDO/2 parameters. Agreement

Table 1. Relative proton affinities (kcal/mole).

Species	$\Delta V(\text{theo})$	$\Delta R(\text{theo})$	$\Delta PA(\text{theo})$	$\Delta PA(\text{expt})$
<u>Acid anions</u>				
CH_3CO_2^-	(0)	(0)	(0)	(0)
$\text{CH}_2\text{FCO}_2^-$	9.5	0.2	-9.3	-10.8
$\text{CH}_2\text{ClCO}_2^-$	9.8	-2.3	-12.1	-12.8
$\text{CHF}_2\text{CO}_2^-$	17.0	0.4	-16.6	-18.0
$\text{CHCl}_2\text{CO}_2^-$	16.4	-3.4	-19.8	-19.8
CF_3CO_2^-	26.6	1.4	-25.2	-25.2
HCO_2^-	11.2	5.9	-5.2	-3.2
$\text{CH}_3\text{CH}_2\text{CO}_2^-$	-0.2	-1.8	-1.6	-1.2
<u>Aliphatic alcohol anions</u>				
OH^-	-	-	27.1	-
CH_3O^-	(0)	(0)	(0)	(0)
$\text{C}_2\text{H}_5\text{O}^-$	-2.7	-4.9	-2.2	-1.9
$i\text{-C}_3\text{H}_7\text{O}^-$	-5.7	-8.8	-3.1	-3.1
<u>Aliphatic alcohols</u>				
CH_3OH	(0)	(0)	(0)	(0)
$i\text{-C}_3\text{H}_7\text{OH}$	-2.5	-10.3	12.8	13

with experiment is remarkably good for relative acidities of substituted acetic acids (Fig. 1). A straight line fits the points to within one Kcal or less, while the standard between theory and experiment is 0.9 Kcal.

Fig. 1. Proton affinities, relative to acetate ion, of chloro- and fluoro-acetic acids, showing excellent agreement between theory and experiment. (XBL 761-2019)

Our results indicate that the increase of acidity accompanying chlorine or fluorine substitution in acetic acid arises primarily by increasing V , making the neutral ground state potential less attractive to the proton. The extent of this effect is apparently about equal for fluorine and chlorine substitution. There are nearly equal contributions to this change in V from both the local and through-space components of the inductive term. That is, the potential at the proton site becomes less attractive both because of a reduction of negative charge on the oxygen and because of a less attractive potential component arising through contributions from other atoms. In these molecules the ΔR term is typically 20% or less of the ΔV term. Within this context the chlorine and fluorine derivatives differ in a significant way. The ΔV and ΔR terms reinforce each other in the chlorine derivatives. Upon deprotonation the chlorine derivatives are able to attract more electronic charge from the proton site (relative to acetic acid); i.e., the chlorine atom's inductive strength is effectively increased. In fluorine derivatives the ΔR term is negligible, implying that the intrinsically equivalent inductive power (relative to chlorine) of fluorine is not enhanced by deprotonation.

A very different situation is obtained for aliphatic alcohols, acids, and amines in which there are no halogen substituents. With one exception (the $\text{HCOOH}-\text{CH}_3\text{COOH}$ acidity shift), the ΔR term is dominant. The reason for this is clear. The al-

iphatic ligands are not polar, and variations in the inductive power from one such ligand to another is small: hence the small ΔV values. The ability of an alkyl group to screen the proton charge depends largely on its size: through delocalization, the larger groups remove the excess positive (or negative) charge farther away from the site of protonation (or deprotonation). In most of the aliphatic alcohols and acids ΔV and ΔR have the same sign. Hence the range of basicities exceeds the acidity range for these compounds ($\Delta\text{PA} = -\Delta V - \Delta R$ for basicity, $\Delta\text{PA} = -\Delta V + \Delta R$ FOR ACIDITY).

By conceptually separating the ΔPA values into ΔV and ΔR terms, it is possible in certain cases to make empirical estimates of the inductive (ΔV) and polarization (ΔR) effects. Consider the aliphatic alcohols, for example. An alcohol has two proton sites: the acid proton site and the basic proton site, from which a proton is lost in the reaction

or gained in the reaction

respectively. If the group is altered the OH group may gain or lose electronic charge by inductive effects, which can be shown to be about twice as large for the latter case.

In contrast, the ΔR_a and ΔR_b terms will be similar. This is apparently a consequence of the ability of a given substituent group to delocalize an excess or a shortage of electronic charge with about equal facility. At any rate, it is found to be approximately true in the detailed PPM calculations.

Combining the changes in PA values for both acid and base protons of a given alcohol as the R group is varied.

$$\Delta\text{PA}_a = -\Delta V_A(1) + \Delta R_a$$

$$\Delta\text{PA}_b = -\Delta V_N(0) - \Delta R_b$$

with the above approximations ($\Delta R_a \approx \Delta R_b$, $\Delta V_A(1) \approx 2 \Delta V_N(0)$), we find

$$\Delta V_N(0) = -\frac{1}{3} (\Delta\text{PA}_a + \Delta\text{PA}_b)$$

$$\Delta V_A(1) = -\frac{2}{3} (\Delta\text{PA}_a + \Delta\text{PA}_b)$$

$$\Delta R_a = \Delta R_b = \frac{1}{3} \Delta\text{PA}_a - \frac{2}{3} \Delta\text{PA}_b.$$

Table 2 presents, along with CNDO/2 estimates, empirical potential energies ΔV and ΔR for nonpolar alcohols. Very good agreement is obtained between the CNDO/2 values and the empirical estimates. As expected, the larger substituents have larger polarization energies. It is expected that this model will extract accurate measures of relative inductive and polarization strengths of nonpolar substituents in alcohols, amines, etc., and qualitative informa-

Table 2. Inductive and polarization effects in aliphatic alcohols from an empirical model and CNDO/2 estimates (kcal/mole).

	CNDO/2				Empirical		
	$\Delta V(0)$	$\Delta V(1)$	ΔR_{ANION}	$\Delta R_{\text{NEUTRAL}}$	$\Delta V(0)$	$\Delta V(1)$	ΔR
CH ₃ OH	0.	0.	0.	0.	0.	0.	0.
CH ₃ CH ₂ OH	-1.5	-2.7	-4.9	-5.8	-1.6	-3.2	-5.4
(CH ₃) ₂ CHOH	-2.5	-5.7	-8.8	-10.3	-3.3	-6.6	-9.7

tion for very polar substituents, e.g., halogens, in these compounds.

* Present address: State of California Air Resources Board, El Monte, CA.
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21. RESEARCH PLANS FOR CALENDAR YEAR 1977

David A. Shirley and Associates

The discovery of new phenomena in electron spectroscopy is still tightly coupled to the development of new experimental techniques. In 1977 we expect to concentrate our photoelectron spectroscopy program around four main experimental projects.

The new magnetic photoelectron spectrometer should be commissioned early in 1977, and brought into multichannel operation during the year. Metals and alloys will be studied in the liquid state, to determine the effect of loss of long-range order on the electronic densities of states. Molecular-beam operation will be developed, to study molecular orbital structures of exotic species, such as Van der Waals' molecules, in collaboration with Y. T. Lee.

A new ultrahigh vacuum spectrometer will be built, based on a movable hemispherical analyzer, for angle-resolved photoemission studies of surfaces and adsorbates. This spectrometer will employ both laboratory radiation sources and synchrotron radiation, and it will be used together with the existing ultrahigh vacuum machines. Among the specific scientific goals of this program will be the elucidation of directional effects in bulk photoemission, the characterization of surface densities of states, and the study of electronic structures in chemisorbed molecules.

Absorption and emission studies of gases using synchrotron radiation at SSRP will be continued and expanded. Photoemission experiments may be initiated. Scientific goals of the absorption and emission experiments will include studies of specific de-excitation paths, including the effects of vibrational relaxation. Photoemission experiments will be aimed at studying shape resonances and autoionization phenomena.

Planning will continue for a new beam line—Beam Line III—at SSRP. Among the major experiments planned for this beam line will be the study of K absorption-edge phenomena in the light elements, as well as extended x-ray absorption fine structure beyond the K edge.

22. 1976 PUBLICATIONS AND REPORTS

David A. Shirley and Associates

Journals

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3. R. L. Martin and D. A. Shirley, Theory of Core-Level Photoemission Correlation State Spectra, J. Chem. Phys. 64, 3685 (1976).
4. R. L. Martin, B. E. Mills, and D. A. Shirley, Fluorine 1s Correlation States in the Photoionization of Hydrogen Fluoride: Experiment and Theory, J. Chem. Phys. 64, 3690 (1976).
5. M. S. Banna and D. A. Shirley, Molecular Photoelectron Spectroscopy at 132.3 eV: N₂, CO, C₂H₄, and O₂, J. Elec. Spect. and Rel. Phen. 8, 255 (1976).
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15. F. R. McFeely, J. Stöhr, G. Apai, P. S. Wehner, and D. A. Shirley, d-Orbital Directed Photoemission from Silver and Gold, *Phys. Rev. B* **14**, 3273 (1976).

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17. J. Stöhr, G. Apai, P. S. Wehner, F. R. McFeely, R. S. Williams, and D. A. Shirley, Angle-Resolved Photoemission from Valence Bands of Cu and Au Single Crystals Using 32-200 eV Synchrotron Radiation, *Phys. Rev. B* **14**, 5144 (1976).

LBL Reports

1. D. W. Davis and D. A. Shirley, Relative Gas-Phase Acidities and Basicities from a Proton Potential Model, LBL-4584.

2. G. Apai, P. S. Wehner, J. Stöhr, R. S. Williams, and D. A. Shirley, Photoemission from CO on Pt(111) Using Synchrotron Radiation in the Range 40 eV $\leq h\nu \leq$ 150 eV, LBL-5122.

3. S.-T. Lee, R. A. Rosenberg, E. Matthias, and D. A. Shirley, Glow Discharge Lamps as Electron Sources for Electron Impact Excitation, LBL-5127.

4. S. P. Kowalczyk, L. Ley, F. R. McFeely, and D. A. Shirley, X-ray Photoelectron Spectroscopic Studies of Transition Metal Difluorides, LBL-5148.

5. S. P. Kowalczyk, F. R. McFeely, L. Ley, V. T. Gritsyna, and D. A. Shirley, The Electronic Structure of SrTiO_3 , and Some Simple Related Oxides (MgO , ZnO , Al_2O_3 , SrO , TiO_2), LBL-5180.

6. B. E. Mills and D. A. Shirley, X-ray Photoemission Spectra of the 2s Valence Orbitals in Cyclic Alkanes in Relation to Valence Bands of Amorphous Group IV and V Elements, LBL-5195.

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Total and Differential Photoemission Cross Sections of Neon, LBL-5413.

8. G. Apai, J. Stöhr, R. S. Williams, P. S. Wehner, S. P. Kowalczyk, and D. A. Shirley, Angle Resolved Photoemission from Cu Single Crystals Using AlK α Radiation, LBL-5489.

9. S.-T. Lee, Ş. Süzer, E. Matthias, R. A. Rosenberg, and D. A. Shirley, Configuration Interaction Effects in the Atomic Photoelectron Spectra of Ba, Sm, Eu, and Yb, LBL-5703.

10. P. S. Wehner, J. Stöhr, G. Apai, F. R. McFeely, and D. A. Shirley, Evidence for d-Orbital Directed X-ray Photoemission, LBL-5713.

11. S. P. Kowalczyk, G. Api, G. Kaindl, F. R. McFeely, L. Ley, and D. A. Shirley, An X-ray Photoemission Investigation of the Density of States of $\beta'\text{NiAl}$, LBL-5744.

12. Steven P. Kowalczyk, Photoelectron Spectroscopy and Auger Electron Spectroscopy of Solids and Surfaces (Ph.D. thesis), LBL-4319.

13. Şefik Süzer, High Temperature UV Photoelectron Spectroscopy, (Ph.D. thesis), LBL-4922.

14. Richard W. Streater, Domain Hyperfine Fields in Some Dilute Ferromagnetic Alloys Studied by NMR on Oriented Nuclei, (Ph.D. thesis), LBL-4981.

15. Bernice E. Mills, Chemical Applications of X-ray Photoelectron Spectroscopy, (Ph.D. thesis), LBL-5123.

16. Richard L. Martin, Many-Electron Effects on Photoelectron Spectroscopy, (Ph.D. thesis), LBL-5167.

17. Fenton Read McFeely, Relaxation and Cross Section Effects in Valence Band Photoemission Spectroscopy, (Ph.D. thesis), LBL-5414.

1976 Invited Talks

1. "XPS Studies of Deep and Shallow Core Levels in Metals", D. A. Shirley, Midwinter Solid-State Research Conference, Laguna Beach, California, January 15, 1976.

2. "Electron-Correlation Satellites in Photoelectron Spectra", D. A. Shirley, Second International Conference on Inner Shell Ionization Phenomena, Freiburg, Germany, April 1, 1976.

3. "Looking Outward from the Nucleus", D. A. Shirley, American Chemical Society Centennial Meeting, New York, New York, April 6, 1976.

4. "Angle-Resolved Photoemission from Metals and Adsorbate Molecular Orbital Spectra", D. A. Shirley, Fifteenth Industrial Affiliates Symposium, Stanford University, Stanford, California, June 15, 1976.

5. "Electron Correlation in Atoms from Photoelectron Spectroscopy", D. A. Shirley, Fifth International Conference on Atomic Physics, Berkeley, California, July 29, 1976.

6. "Electronic Structures of Surfaces and Adsorbates from Photoelectron Spectroscopy", D. A. Shirley, Surface Science and Catalysis Seminar, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, CA, October 8, 1976.

7. "Science of Materials at a Large University Center", D. A. Shirley, presented to the Fall Meeting of the Solid State Sciences Council of the

National Academy of Sciences, Washington, D.C., December 16, 1976.

8. "Photoemission Studies of Cross Section Effects and Surface Sensitivity Using $32 \text{ eV} \leq h\nu \leq 250 \text{ eV}$ ", J. Stöhr, Winter Meeting of the American Physical Society, Stanford University, Stanford, CA, December 22, 1976.

g. Crossed Molecular Beams

Yuan T. Lee, Principal Investigator

1. SCATTERING OF Ar*, Kr* WITH Xe

K. Shobatake

We have carried out a cross beam experiment of metastable argon and krypton with xenon. The metastable Ar* (or Kr*), the mixture of Ar (3P_2) and Ar (3P_0), was produced by crossing 100 to 150 eV electron beam perpendicularly to a supersonic argon beam.¹ The secondary beam of xenon in the ground state 1S_0 was also a supersonic beam with FWHM velocity distribution 17-19%. The elastically scattered metastable atoms were measured by using a detector which moves around the scattering center in the same plane of two beams. The differential cross sections of Ar* and Kr* + Xe at collision energies $\bar{E}$ of 1.46 and 1.47 kcal/mole are shown in Fig. 1. The direction

(up to 20 degrees), and then the best-fit opacity function P_ℓ as a function of orbital angular momentum $\hbar\ell$ was obtained so that the best-fit of the calculated angular distribution to the observed one is reached in the whole laboratory angle range. The best-fit potential $V(R)$ so obtained is shown in Fig. 2. In Fig. 3 the

Fig. 1. Differential cross sections for Ar*($^3P_{2,0}$) and Kr*($^3P_{2,0}$) + Xe at nominal collision energies of 1.46 and 1.47 kcal/mole. The solid curves represent the best-fit distributions calculated by applying the optical potential model and the dashed ones are the elastic distributions calculated by using only the van der Waals potential $V(R)$. (XBL 7611-9889)

of the metastable beam corresponds to $\theta = 0^\circ$, and that of xenon beam to $\theta = 90^\circ$. The differential cross sections for both systems were analyzed by applying the optical potential model.²

The van der Waals part of the spherical symmetric potentials have been determined by fitting the low angle differential cross sections

Fig. 2. Best-fit potential $V(R)$ for Ar* and Kr* + Xe. (XBL 7611-9887)

Fig. 3. Opacity function P_ℓ plotted against the impact parameter b . The corresponding ℓ scales are also shown. (XBL 7611-9888)

Table 1. Best-fit Potential Parameters and Quenching Cross Sections for Ar* and Kr* + Xe System and Relevant Literature Values

(1) Potential Parameters ϵ and r_m for X + Xe						
X =	Ar*	Kr*	K	Cs	Ar	
ϵ (kcal/mole)	0.281	0.282	0.317	3.14	0.378	
r_m (Å)	5.25	5.35	5.25	5.47	4.10	
Reference	present work		a	a	b	

(2) Quenching Cross Section σ_Q for X + Xe						
X =	Ar*	Kr*	Ar* ^c	Ar(³ P ₂) ^c	Ar(³ P ₀) ^c	Kr(³ P ₂) ^c
σ_Q (Å ²)	43	43	46	50	58	100 ± 30
E (kcal/mole)	1.46	1.47	0.75	0.75	0.75	1.26
Reference	this work		4	5	5	6

^aU. Buck and H. Pauly, Z. Physik. 208, 390 (1968).
^bJ. M. Parson, T. P. Schafer, P. E. Siska, F. P. Tully, Y. C. Wong, and Y. T. Lee, J. Chem. Phys. 53, 3755 (1970).
^cEstimated by dividing the quenching rate k_0 by the mean Boltzmann speed $\bar{v}$ as $\sigma_Q = k_0/\bar{v}$. The collision energy $\bar{E}$ is simply calculated by $\bar{E} = \mu\bar{v}^2/2$ where μ is the reduced mass.

opacity function is plotted as a function of the impact parameter $b = (\ell + 1/2)\hbar/\mu\bar{v}$, where μ is the reduced mass and $\bar{v}$ is the relative collision velocity. The best-fit potential parameters, ϵ and r_m and the quenching cross sections σ_Q are summarized in Table 1. The calculated best-fit angular distributions are shown in solid curves and the dotted curves represent the calculated angular distributions using only the potential $V(R)$. The small hump at 40° and 82° for Ar* + Xe system has been assigned to metastable Xe atoms which are produced through the excitation transfer process by Martin et al.³ As shown in Table 1, the quenching cross section obtained for Ar* + Xe system 43 Å² is in good agreement with those obtained by non-beam experiments.^{4,5} For Kr* + Xe system our cross section 43 Å² is smaller than that determined by Bochkova and Kuznetsova.⁶ The potential well depth ϵ 's are found to be smaller than those corresponding alkali atom-Xe pair by about 11%, but r_m 's are comparable to those of alkali atom - Xe pair.

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2. METASTABLE RARE GAS INTERACTIONS, He* + H₂

Z. F. Wang

With the demonstration of potentially high power lasers from excimer systems, and more recently the exciting discovery of some related laser-grade reactions typified by those involving Xe* and halogen containing compounds,¹ on-going efforts to understand metastable rare gas chemistry have gained much additional impetus. When a rare gas atom approaches another atom or molecule, it does so on a unique potential surface. It follows that an accurate characterization of this potential is essential to the complete understanding of the fundamental

processes at work. Our group has been applying molecular beam techniques to extract this very important piece of information.²

One particular combination of rare gas atom and molecule we have fairly extensively looked into is $\text{He}^* + \text{H}_2$. This system has a number of desirable qualities in its favor: (a) It has sufficiently few electrons as to permit one to model it theoretically from first principles.³ (b) The interaction becomes inelastic or reactive only at small impact parameters. This, as will be explained presently, greatly aids in the analysis of the corresponding differential cross section data. (c) The rotational and vibrational levels in H_2 are quite widely spaced, so that perturbations on the respective population distributions by He^* under normal beam conditions are expected to be very small.⁴ We can therefore concentrate on just the various ionization process involved without having to worry about other complications.

The interaction potential is phenomenologically treated as composed of a real and an imaginary part.⁵ The former determines the trajectory on which the reaction proceeds, while the latter accounts for the loss of reactants. Differential cross section measurements under favorable conditions can provide a handle on both contributions. In the case of $\text{He}^* + \text{H}_2$, since only the small impact parameters are conducive to reaction, one would see a discernible drop in the elastic differential cross section only at large angles, thus the small-angle-values and the information contained therein about the real par of the potential are left unscathed.

We have obtained the differential cross section at three temperatures spanning the range of 0.8 kcal/mole to 2.6 kcal/mole in center-of-mass energy. The intensities of the various species of ions produced at each collision energy are also monitored. The energy dependence of the sum production of these ions should mirror that of the total reactive cross section. A self-consistent MMSV type potential has been fitted to the three aforementioned sets of differential cross sections, and the parameters are listed in Table 1.

MMSV potential:

$$\begin{aligned} f(x) &= \exp[-2_1(x-1)] - 2\exp[-_1(x-1)], & x_1 < x \leq 1 \\ f(x) &= \exp[-2_2(x-1)] - 2\exp[-_2(x-10)], & 1 < x \leq x_2 \\ f(x) &= b_1^{+(x-x_2)} b_2^{+(x-x_3)} [b_3^{+(x-x_2)} b_2] , & x_2 < x \leq x_3 \\ f(x) &= c_6 x^{-6} - c_8 x^{-8}, & x_3 < x \leq \infty \end{aligned}$$

where

$$f(x) = V(4)/\epsilon; \quad x = r/r_m; \quad c_n = C_n/\epsilon r_m^n. \quad (1)$$

It is to be observed that the major source of uncertainty is found in the shape of the repulsive wall. Since the latter primarily scatters to large angles, a range in which the influence of the imaginary potential is quite strong, it is clear that different combinations of the

Table 1. MMSV Potential Parameter.

ϵ (kcal/mole)	0.0285
r_m (Å)	6.4
β_1	7.5
β_2	5.9
C_6 (kcal/mole Å ⁶)	250
C_8 (kcal/mole Å ⁸)	2700
b_1	-0.75
b_2	1.1332
b_3	-3.979
b_4	3.47
x_1	0
x_2	1.0924
x_3	1.75

repulsive slope and the imaginary potential can conceivably still fit the data. This ambiguity can be removed in one of two ways:

(1) Differential cross section measurements can be taken over a wide range of center-of-mass energies, a task which is formidable in terms of experimental implementation. (2) For the same range of energies, the total reactive cross section can be monitored. It has been shown that the energy dependence of the total reactive cross section imposes tight constraints on which imaginary potential is acceptable.⁶

For $\text{He}^* + \text{H}_2$, neither (1) nor (2) is available. Only rate constants covering a substantial range of temperatures have been measured;⁷ these values are necessarily highly averaged representations of the total cross sections, and as such cannot uniquely determine a potential. Indeed, agreement with them are at best corroborative but never conclusive. Nevertheless, the rate constants calculated from our potential obtained via the differential cross section data agree very well with the experimental values of Lindinger, et al.⁷

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3. AN ATOMIC AND MOLECULAR HALOGEN BEAM SOURCE

James J. Valentini and Michael J. Coggiola

We have constructed¹ a supersonic nozzle beam source which can be used to produce beams of halogen molecules, or halogen atoms by thermal dissociation. The source employs a graphite nozzle which can be heated to temperatures above 2000 K to produce beams of chlorine, bromine, or iodine molecules or atoms seeded in rare gas diluents. By varying the rare gas diluent, beams with energies from a few hundredths of an eV to several eV have been produced. This source has been used for crossed beam studies of reactive collisions of chlorine molecules and atoms² and elastic scattering of chlorine atoms.³

The nozzle source, shown partially sectioned in Fig. 1, is resistively heated by low voltage,

Fig. 1. Partially sectioned view of graphite nozzle source. A--water cooling lines for O-ring cooling block; B--nozzle retaining plate; C--springs; D--water cooling lines for support block; E--copper support block; F--graphite sleeve; G--water cooling channel; H--copper mounting block; I--outer graphite tube; J--tantalum radiation shield; K--inner graphite tube; L--graphite retaining nut; M--mica insulation; N--Cajon ultratorr fitting; O--copper O-ring cooling block; P--water cooling lines for mounting block; Q--gas inlet line.

(XBL 768-10150)

high current AC power (up to 7 volts rms and 450 amps). Figure 2 is an enlarged and simplified axially sectioned view of the source showing the heating current path.

The outer graphite tube and nozzle are machined from a special high-density graphite. The nozzle orifice (0.079 mm) is hand drilled after final machining. The outer graphite tube (2.22 cm O.D., 0.32 cm wall) is screwed into the copper mounting block and a graphite nut is screwed onto the tube and tightened down against the copper mounting block to hold the outer graphite tube firmly in place. The nozzle itself (1.27 cm O.D., 0.32 cm wall) is supported at two points. At the front it fits snugly into the conical bore of the outer graphite tube. At the rear it is

Fig. 2. Heating current paths for graphite nozzle. E--copper support block and current return; F--graphite sleeve; H--copper mounting block and current supply; I--outer graphite tube; K--inner graphite tube; L--graphite retaining nut.

(XBL 768-8979)

securely mounted in a two piece copper supporting block which is split along the axis of the nozzle. The two halves of the supporting block are tightened down on the two halves of a cylindrical graphite sleeve in which the nozzle can slide. This arrangement gives stable support to the nozzle while allowing axial movement due to thermal expansion of the nozzle upon heating. The nozzle supporting block is rigidly fixed to the copper mounting block by means of two screws which are electrically insulated from the mounting block by mica washers and teflon sleeves. The supporting block and mounting block are separated by several thicknesses of mica sheet.

At its end the nozzle is attached to a 0.32 cm O.D. stainless steel gas feed line by means of an "O"-ring type fitting. A thin copper plate is attached to the rear of this fitting, and two steel springs connecting the plate to the copper supporting block apply a small axial force to the nozzle. This spring loading keeps the nozzle firmly seated in the conical bore of the outer graphite tube, despite thermal expansion and contraction of the nozzle when repeatedly heated and cooled. The gas feed line is wound in a large radius helix to allow for the expansion and contraction of the nozzle.

Velocity distributions of seeded beams of halogen atoms and molecules produced by expansion from the graphite nozzle have been determined from time-of-flight velocity analysis. Figure 3 shows the variation of the peak flux velocities for chlorine atoms, chlorine molecules, and diluent gas as a function of nozzle temperature for various seeded mixtures. The accessible range of particle energies for this source using these seeded mixtures is quite large. For chlorine atoms energies as low as 0.10 eV and as high as 0.14 eV are possible. For chlorine molecules the energy range is even wider, from 0.02 to 2.2 eV. The performance of the graphite nozzle as a source of bromine molecules and atoms has also been evaluated. Figure 4 shows the variation of peak flux velocities as a function of temperature for all species in a 6.3% Br₂ in Ar mixture. This mixture was generated by passing the argon diluent gas through a temperature controlled reservoir containing liquid bromine.

Fig. 3. Peak flux velocities for chlorine atoms (■), chlorine molecules (●) and diluent gas (▼) as a function of source temperature for three seeded gas mixtures. Solid curves indicate expected velocity dependence assuming an ideal seeded beam expansion. (XBL 767-3100)

Fig. 4. Peak flux velocities for bromine atoms (■), bromine molecules (●) and diluent gas (▼) as a function of source temperature. The seeded mixture was 6.3% Br_2 in Ar. The solid curve shows the expected velocity dependence assuming an ideal expansion. (XBL 767-3097)

Bromine atom and molecule energies of approximately 0.3 eV to 0.5 eV can be produced with this nozzle and seed gas mixture. By using mixtures of bromine in xenon and helium with this source bromine atom (molecule) energies from 0.08 eV to ~2.0 eV (0.4 eV to ~3.3 eV) are accessible.

The velocity distributions of the seeded halogen beams produced with the source are quite narrow, 6-15% FWHM, corresponding to Mach numbers of 15 to 7.

Halogen atom or molecule intensities of 10^{17} to 10^{18} particles/sec-sr are typically obtained.

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4. A CROSSED MOLECULAR BEAM STUDY OF THE $\text{Cl} + \text{Br}_2 \rightarrow \text{BrCl} + \text{Br}$ REACTION

James J. Valentini and Daniel J. Auerbach

We have completed¹ a crossed molecular beam study of the $\text{Cl} + \text{Br}_2 \rightarrow \text{BrCl} + \text{Br}$ reaction at several collision energies. Angular distributions as well as velocity distributions of the scattered BrCl product have been measured. Figures 1, 2, and 3 show the center-of-mass contour maps of product flux constructed from the angular and velocity distribution data.

Fig. 1. Contour map of BrCl flux density in the center-of-mass coordinate system produced in the reaction $\text{Cl} + \text{Br}_2$ at a collision energy of 6.8 kcal/mole. (XBL 7611-9716)

Fig. 2. Contour map of BrCl flux density in the center-of-mass coordinate system produced in the reaction $\text{Cl} + \text{Br}_2$ at a collision energy of 14.7 kcal/mole. (XBL 7611-9718)

Fig. 3. Contour map of BrCl flux density in the center-of-mass coordinate system produced in the reaction $\text{Cl} + \text{Br}_2$ at a collision energy of 17.7 kcal/mole. (XBL 7611-9717)

The contour maps of Figs. 1-3 show quite clearly that the BrCl product peaks almost exclusively in the forward hemisphere, even at the lowest collision energy. The contour maps show that the c.m. angular spread of the BrCl product does not change very much, even when the collision energy is increased from 6.8 kcal/mole to 17.7 kcal/mole. However, as the collision energy is increased the spread of the BrCl product in recoil velocity decreases quite sharply.

The change in the form of the recoil energy distribution is shown in detail in Fig. 4. This figure gives plots of the relative intensity, $P(E_T'/E_{TOT})$, as a function of the fraction of the total available energy, E_{TOT} , which appears in translational energy of the products, E_T' .

Fig. 4. ● Product recoil energy distributions for the $\text{Cl} + \text{Br}_2$ reaction at collision energies of 6.8 kcal/mole, 14.7 kcal/mole, and 17.7 kcal/mole, as a function of the fraction of the total available energy, obtained by angle averaging $I_{c.m.}(\theta, E_T')$, see text. (XBL 7611-4783)

$$P(f) = P(E_T'/E_{TOT}) = \sum_{\theta} I_{c.m.}(\theta, E_T') = \sum_{\theta} I_{c.m.}(\theta, u)/u,$$

where $I_{c.m.}(\theta, u)$ is the center-of-mass flux distribution as shown in Figs. 1, 2, or 3. These distributions show that when averaged over recoil angle, the recoil energy distributions do not peak at energies which are very different. In all cases the distributions peak at approximately 0.14 to 0.18, i.e., 14% to 18% of the total available energy. However, these recoil energy distributions do show a dramatic change as the collision energy is increased. At the lowest collision energy the recoil energy distribution is quite broad, extending to the nominal kinematic limit, $E_T'/E_{TOT} = 1$. As the collision energy is increased the recoil energy distribution becomes sharper, and the amount of product which

appears with a large amount of translational energy decreases dramatically.

The average product translational energy,

$$\bar{E}_T = \frac{\sum_{E_T'} P(E_T') \cdot E_T'}{\sum_{E_T'} P(E_T')},$$

is, however, a considerably larger fraction of the total energy, ~38%, for the lowest collision energy, than for the higher collision energies, ~22%. This is of course due to the much greater range of recoil energies for the lowest collision energy than for the higher energies, even though the peak recoil energy is about the same fraction of the total energy for each case.

It is clear that the increased sharpness of the BrCl lab angular distributions at higher energy is a consequence of the narrower recoil energy (velocity) distributions at higher energies, and not an increasingly sharp center-of-mass angular distribution. As can be seen in Fig. 5 the center-of-mass angular distributions,

$$I(\theta) = \sum_{E_T'} I_{C.m.}(\theta, E_T')$$

are nearly identical at all three collision energies.

Fig. 5. ○ Center-of-mass angular distributions of BrCl produced in the Cl + Br₂ reaction at collision energies of 6.8 kcal/mole, 14.7 kcal/mole, and 17.7 kcal/mole, obtained by averaging $I_{C.m.}(\theta, E_T')$ over recoil energy. (XBL 7611-4784)

We have also made an attempt to determine the total reactive cross section, σ_R , for the Cl + Br₂ reaction at these collision energies. This was done by comparing the integrated intensity of reactive scattering to the observed intensity of small angle elastic scattering of chlorine atoms from bromine, which was normalized to the theoretical small angle elastic scattering intensity from theoretical van der Waals force constants.

The result of this calculation at collision energies of 6.8 kcal/mole and 14.7 kcal/mole gives $\sigma_R = 11 \text{ Å}^2$ and $\sigma_R = 14 \text{ Å}^2$ respectively. These numbers are probably only accurate to within a factor of three due to uncertainties attendant to the calculation of the total cross section in this manner.

The results of this work and the results²⁻⁴ of an investigation of this reaction at lower collision energy (~3.0 kcal/mole) seem to indicate that the Cl + Br₂ reaction occurs on an attractive energy surface without any appreciable activation energy or barrier. Although the Cl + Br₂ interaction seems to be an attractive one, the total reactive cross sections are much smaller than hard sphere values. The sharp recoil energy distribution at the highest collision energy, peaking at 14% of the total available energy, seems to indicate that the reaction is approaching the spectator stripping model, which predicts a unique recoil translational energy, 11% of total available energy at this collision energy.

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5. O(³P) REACTION DYNAMICS: DEVELOPMENT OF THE HIGH PRESSURE PLASMA BEAM SOURCE

Steven J. Sibener

The reactions of ground-state oxygen atoms are of considerable interest and importance due to their fundamental role in combustion processes and atmospheric chemistry. A high pressure (supersonic) radio frequency discharge beam source has been developed in order to determine the products and reaction dynamics of these reactions utilizing crossed molecular beam techniques. Previous crossed beam studies of O + halogen molecules, by the groups at both Harvard¹ and Cambridge,² have used low pressure (effusive) discharge sources having Maxwell-Boltzmann velocity distributions. The gain in beam intensity and the narrowing of the beam velocity spread due to the high pressure beam expansion is necessary in order to study O(³P) reactions with unsaturated hydrocarbons.

The attainment of a stable high pressure discharge is much more difficult than sustaining a low pressure (~1 Torr) discharge. Impedance matching of the plasma as a function of both pressure and gas composition is required. Also, sufficient cooling of the nozzle in order to prevent meltdown--while not interfering with power coupling to the plasma--is mandatory.

Finally, plasma localization directly behind the orifice is required in order to limit atomic recombination before the expansion.

The impedance matching of the RF to the inductively coupled plasma was achieved by using a modified PI-network³ circuit in conjunction with an autoformer arrangement in the final tank (plasma coupling) circuit. Standing wave ratios of less than 1.05:1 are now readily achieved. The cooling problem was overcome by flowing deionized water in a jacket separating the tank coil from the plasma containing region. This served a three-fold purpose: meltdown of the quartz was prevented, atomic recombination at the surface of the quartz was reduced, and arcing was inhibited due to the low conductivity of the deionized water. Plasma localization has been achieved and amplifier power levels in excess of 1000 watts are now available.

Preliminary elastic scattering experiments ($O + He$) have been carried out in conjunction with time-of-flight measurements. The experimentally determined differential elastic cross sections are shown in Fig. 1 for both O -He and

Fig. 1. Differential elastic cross sections for O -He and O_2 -He. The wide angle behavior (20-50 degrees) of the O -He cross section clearly confirms $O(^3P)$ production. (XBL 7611-9782A)

O_2 -He. Dissociation on the order of 90% is indicated for a 5% O_2/Ar mixture discharged at 95 Torr by 95 watts. The diluting effect of the Ar carrier gas permits operation at higher beam pressures since atomic recombination is reduced. Mach numbers of 4-7 have been measured in these studies. The plasma temperature is found to be on the order of 1300 K.

In the immediate future beam optimization will be completed and reactive experiments involving unsaturated hydrocarbons, halogens and CS_2 will commence. In particular, the direct detection of bimolecular collision products for $O +$

hydrocarbon reactions will hopefully clarify the reaction mechanism of these systems.⁴

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6. ENERGY RANDOMIZATION IN THE $Cl + C_2H_3Br \rightarrow Br + C_2H_3Cl$ REACTION

M. J. Coggiola and R. J. Buss

When unimolecular processes are studied under single collision conditions, product energy distributions can yield information about the reaction dynamics. In chemiluminescence experiments with the reaction

Durana and McDonald¹ found a product vibrational energy distribution which was inconsistent with a complete randomization of energy in the intermediate complex. On the other hand, Cheung et al.² found in crossed molecular beam experiments that the product translational energy distribution for this reaction agreed with predictions based on a statistical model. This apparent contradiction in product energy distributions led us to study the reaction using crossed supersonic beams with relatively low velocity spreads.

The chlorine atoms were produced in a resistively heated graphite oven from a mixture of 10% Cl_2 in argon. The velocity distribution of the chlorine atoms corresponded to a nozzle temperature of 1496 K and a mach number of 9.0. The secondary beam was pure vinyl bromide expanding from a room temperature nozzle. The average collision energy was 6.3 kcal/mole. The vinyl chloride product, detected at mass 62.0, was velocity analyzed by cross correlation time-of-flight.

The angular distribution, shown in Fig. 1, indicates a strong peak 10 degrees from the chlorine beam. This corresponds to vinyl chloride scattered forward with respect to the incoming chlorine atom. The backward scattered product would be expected to peak beyond the secondary beam, outside the range of our detector. It is, therefore, not clear whether the lifetime of the complex exceeds the rotational period. Time-of-flight data were taken throughout the angular range and combined with the angular data to give the contour map shown in Fig. 2. The contours are center-of-mass product flux which have been deconvoluted to remove effects of machine resolution. The pronounced peaking on the relative velocity vector is expected for this reaction in which orbital angular momentum should be large for both reactants and products.

Fig. 1. Angular distribution of reactively scattered C_2H_3Cl . (XBL 7612-10988)

Fig. 2. Center-of-mass contour map of the C_2H_3Cl product flux. (XBL 7612-10987)

We were able to obtain a product translational energy distribution which fits the time-of-flight data at all center-of-mass angles. This is shown in Fig. 3 with the results of two statistical calculations.

In the reaction under consideration most complexes will have large angular momenta. Thus

a significant fraction of the collision energy will appear as product translational energy. Safron et al.⁵ have developed a modification of RRKM theory which accounts for angular momentum in the case of "loose complex" formation. This reaction which is characterized by a negligible potential barrier in both entrance and exit channels and possesses a large total cross section would be placed in the loose complex category. RRKM calculations with the angular momentum correction included produced energy distributions substantially different from the experimental results. The calculation, labeled 12 ocs. in Fig. 3, in which all vibrations are

Fig. 3. Experimental (solid line) and calculated (dashed line) product translational energy distributions for the reaction $Cl + C_2H_3Br$. (XBL 7612-10986)

assumed to share the available energy in the complex is much narrower and peaks at lower energy than the observed distribution. Also shown is a calculation in which only the five low frequency modes are assumed to share the energy. Although this change broadens the distributions, it cannot account for the large product energies observed. Thus it would appear that this reaction cannot be treated with a purely statistical model, but there remains some question about the angular momentum treatment. The model of Safron et al. assumes a distribution of angular momenta which depends solely on an attractive force between centers-of-mass of the reactants. A more realistic treatment might favor collisions in which the chlorine attacks the double bond, some distance from the vinyl bromide center-of-mass. The angular momenta of the complexes would be greater, on the average, and the product translational energy distribution consequently shifted upward. This question could be resolved by decreasing the collision energy several kcal, thereby reducing the effect of angular momentum without greatly altering the energetics of the reaction. At present we are limited in our ability to decrease the chlorine velocity but development of an RF discharge source offers some hope for this approach. We intend to investigate related reactions of chlorine with brominated olefins in order to separate the energy randomization question from that of angular momentum disposal.

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7. HIGH RESOLUTION PHOTOIONIZATION STUDIES OF NO AND ICl*

C. Y. Ng and P. W. Tiedemann

In the studies of ionization processes of atoms and molecules, the photoionization technique offers many advantages over the electron impact method. First, all the difficulties that contribute to the instability and poor resolution of the electron impact experiments such as sample pyrolysis due to the hot filament, the presence of space charge due to the electron beam and the effects of charging up the surfaces of the ion optics, are avoided in the photoionization method. Second, the threshold law for photoionization is much more favorable for investigating the ionization potentials of atoms and molecules. The typical instrumental resolution for photoionization is 1-10 meV. However, due to the rotational (and vibrational) temperature of the molecules which is about 30 meV at room temperature, this value of the resolution is essentially unattainable unless the

sample gas is cooled down to the corresponding temperature. The cooling of the gas in a gas cell to, e.g., 77 K (~ 7 meV) in a conventional photoionization experiment is only feasible for a noncondensable gas such as H_2 . Thus, the attainable resolution for condensable gases in photoionization experiments will be limited by their corresponding freezing temperatures. We have overcome this problem by using a supersonic beam technique to introduce the target gases to the ionization region. In an isentropic expansion, individual molecules can be easily supercooled to well below 20 K. This has been demonstrated by the high resolution obtained for the photoionization efficiency curves of NO, and ICl, etc.^{1,2} The analysis of these spectra has yielded ionization potentials for these molecules to an accuracy of ± 3 meV. Detailed autoionization structures were also resolved. This allows the investigation of selection rules for autoionization, and identification of the Rydberg series which converge to the excited state of the molecular ions.

The photoionization efficiency curve of the NO molecule near the threshold is shown in Fig. 1 for illustration. The step-function behavior corresponds to the direct ionization of NO ($^2\Pi_{3/2}, 1/2$) to the different vibrational states of the NO^+ ($X^1\Sigma$) molecular ion. From the height of the steps, relative transition probabilities can be derived. Autoionization structure superimposed on the vibrational steps

Fig. 1. Photoionization efficiency of NO.

(XBL 764-1087A)

can be fit with a Rydberg formula in which only one value of the quantum defect (0.87) is used. In addition, the autoionization structure observed for the first four vibrational steps is found to obey the propensity rule proposed by Berry.³

Fig. 2. Photoionization efficiency of $\text{ICl} + h\nu \rightarrow \text{ICl}^+ + e$. (XBL 767-3242)

Figure 2 shows the photoionization efficiency curve of ICl. The ionization potential of ICl from the ground electronic state ($^4\Sigma^+$, $v''=0$) to ICl^+ ground molecular ionic state ($^2\Pi_{3/2g}$, $v'=0$), was found to be 10.069 ± 0.003 eV which is in agreement with the value obtained by Dibeler, et al. The ionization potential corresponding to the ionization of ICl ($^4\Sigma^+$, $v''=0$) to $\text{ICl}^+(^2\Pi_{1/2g}$, $v'=0$) was found to be 10.699 ± 0.003 eV. By analyzing the photon yield curve of ICl, the vibrational quantum for the $\text{ICl}^+(^2\Pi_{3/2g})$ was deduced to be 428 ± 20 cm^{-1} . The excitation efficiency leading to ion pair formation (i.e., $\text{ICl} + h\nu \rightarrow \text{I}^+ + \text{Cl}^-$) was also observed for ICl by monitoring I^+ atomic ions as was shown in Fig. 3. Using the known electron affinity for

Fig. 3. Photoionization efficiency of $\text{ICl} + h\nu \rightarrow \text{I}^+ + \text{Cl}^-$. (XBL 767-3243)

$\text{Cl}(^2P_{3/2})$ atom the dissociation energy for ICl is deduced to be 2.140 ± 0.003 eV.

*Work carried out in collaboration with Professor Mahan's group.

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8. PHOTOIONIZATION OF $(\text{H}_2\text{O})_n$ AND $(\text{NH}_3)_2$ *

D. J. Trevor, P. L. Kronebusch, and C. Y. Ng

The high degree of rotational relaxation and the low relative translational temperature after supersonic expansion facilitates the condensation process. Water and ammonia clusters formed by this technique were studied by photoionization mass spectroscopy.¹ From this study the well depths of the ion-neutral interactions of $(\text{H}-\text{H}_2\text{O})^+$, $(\text{H}_2\text{O})_2^+$, $(\text{H}-(\text{H}_2\text{O})_2)^+$, and $(\text{NH}_3)_2^+$ were determined.

The water molecular beam was produced by seeding water vapor at 89°C in 150 Torr argon and then expanding through a 0.15 mm diameter nozzle. The photoionization efficiency of water and its dimer at a photon full width band pass of 2.5 Å are shown in Fig. 1. The ion yield curves of

Fig. 1. Photoionization efficiency with a photon resolution of 2.5 Å FWHM, showing H_2O^+ , $(\text{H}_2\text{O})_2^+$ and H_3O^+ signals, scaled for relative signals at 950 Å. (XBL 769-10670)

H_3O^+ and H_5O_2^+ produced by dissociative ionization are shown in Fig. 2.

Fig. 2. Ion yields for H_3O^+ and H_5O_2^+ with photon resolution of 2.5 Å FWHM, same beam conditions. (XBL 769-10671)

The ionization potential of monomeric water was found to be 12.601 ± 0.016 eV and is in excellent agreement with previous studies.² The

step-like structure in the photoionization efficiency is characteristic of direct ionization to higher vibrational levels in the ion. The observed thresholds at 12.790 ± 0.016 eV and 13.011 ± 0.016 eV are assigned to excitation of the ν_2 bending mode and the ν_1 symmetric stretch, respectively. This assignment is made to agree with high resolution photoelectron spectra.² The ionic vibrational frequencies were found to be $\nu_1 = 3300 \pm 260$ cm^{-1} and $\nu_2 = 1520 \pm 260$ cm^{-1} .

Due to low signal no sharp threshold was observed for the water dimer. The ionization potential, 11.21 ± 0.03 eV, is only an upper bound set by the minimum observable signal (0.01 of the maximum signal detected). To obtain the well depth of the ion neutral interaction by this technique the well depth of the neutral-neutral interaction must be known. Measurements of the hydrogen bond dissociation energy reported in the literature vary from 3 to 7 kcal/mole. The most reliable value appears to be 5 ± 1 kcal/mole.³ The difference between the ionization potential of the monomer, 12.615 ± 0.001 eV,¹ and the upper bound to the ionization potential of the dimer is 1.40 ± 0.03 eV (32.4 ± 0.7 kcal/mole). Therefore, the water ion-neutral well depth is at least 1.62 ± 0.07 eV (37.4 ± 1.7 kcal/mole).

The thresholds for the dissociative ionization of water clusters according to the reaction

enable the determination of their respective proton affinities (P.A.), via the cycle (see Fig. 3):

Fig. 3. Summary of thermodynamic data for H_2O , $(\text{H}_2\text{O})_2$, $(\text{H}_2\text{O})_3$ and liquid water. The thick lines represent measured quantities. (XBL 769-10687)

The exoergicity of (1) can be obtained from the hydrogen bond dissociation energy of water. The endoergicity of (2) is the measured dissociative ionization threshold; (3) is obtained from thermodynamic tables as -18.75 eV.⁴ The expectation of OH, not OH⁻, as product is based upon evidence that water monomer does not dissociate via the ion pair channel.⁵ At 11.71 ± 0.03 eV the ion yield of H₃O⁺ quickly drops to a value below the minimum detectable signal (0.001 of maximum signal observed). The calculated proton affinity is 7.26 ± 0.07 eV (167.4 ± 1.7 kcal/mole). This agrees well with previously accepted value of 164 ± 4 kcal/mole.⁶ At 11.21 ± 0.03 eV the H₅O₂⁺ signal fell below the detectable limit (0.001 of the maximum signal observed) but without a rapid decline in intensity. This upper bound to the threshold yields a lower bound to the proton affinity of the dimer, namely, 7.83 ± 0.07 eV (180.5 ± 1.7 kcal/mole).

Ammonia dimer was also studied using a 400 Torr beam expanded through a 0.13 mm diameter nozzle. Its photoionization efficiency is shown in Fig. 4. At 9.10 ± 0.02 eV the (NH₃)₂⁺ signal fell

Fig. 4. Photoionization efficiency of (NH₃)₂⁺ with a photon resolution of 2.5 Å FWHM. (XBL 769-10669)

below the detectable limit (0.005 of the maximum signal observed).

The study of condensates produced in the supersonic expansion of a molecular beam will be extended to larger clusters pending further developments in beam source design.

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9. PHOTOIONIZATION MASS SPECTROSCOPY OF NH₃⁺ AND O₃⁺ *

D. J. Trevor, P. L. Kronebusch, and M. L. Kowalczyk

The high degree of rotational relaxation in a supersonically expanded molecular beam enables accurate determination of ionization potentials as well as vibrational structure of the ionic state. The method used combines photoionization mass spectroscopy with supersonic molecular beam technology. The major components of the apparatus are a vacuum ultraviolet light source and monochromator, a double differentially pumped modulated supersonic molecular beam source, and a quadrupole mass filter with a Daly type ion counting detector.

The experiment is performed by crossing the monochromatic VUV light with the molecular beam which is modulated at 150 Hz. The ions produced in this region are extracted and focused onto the entrance of the QPMS which is perpendicular to the plane of the molecular beam and incident photons. The ion yield is then measured as a function of the incident photon energy. The energy resolution for this technique is limited by the chosen band pass of the monochromator. This distinguishes these studies from those which use effusive sources or gas cell sources; in those experiments the rotational broadening of ~24 meV at room temperature limits the ultimate energy resolution. The photoionization studies reported here showed no sign of rotational broadening due to the high degree of rotational relaxation in the supersonic expansion.

The photoionization efficiency for ammonia expanded through a 0.13 mm diameter orifice at 100 Torr is shown in Fig. 1. The first ionization potentials is determined to be 10.176 ± 0.008 eV. The step-like structure is characteristic of the direct ionization process to excited vibrational

Fig. 1. Photoionization efficiency of NH_3^+ .
(XBL 769-10673)

states of the ion. The vibrational frequency of $950 \pm 32 \text{ cm}^{-1}$ is assigned to the out of plane bending mode of the ion, NH_3^+ . The neutral species, NH_3 , is pyramidal while its ion is believed to be planar. This large change in geometry implies a gradual rise in the photo-

ionization efficiency near threshold which, indeed, is what's observed. These results are in excellent agreement with previous studies of ammonia as shown in Table 1.

The sharp resonance-like structure is indicative of excitation to autoionizing states. This feature, which is predominant in our measurements, was not observed by previous investigators due to rotational broadening which is three times greater than their photon resolution.³ Further improvement of the resolution is necessary before assignment of these autoionizing states can be made.

The photoionization efficiency of Ozone expanded through a 0.15 mm diameter nozzle at a partial pressure of ~10 Torr in 250 Torr Ar is shown in Fig. 2. The ionization potential determined from this study is $12.523 \pm 0.008 \text{ eV}$. The distinctive step-like structure yields a vibrational frequency for the ion of $650 \pm 40 \text{ cm}^{-1}$. This is assigned to the ν_2 bending mode. These values are in excellent agreement with previous studies shown in Table 2. The sharpness of the initial step-like structure is indicative of the high degree of rotational relaxation achieved in the supersonic expansion. At higher energy the steps become more diffuse due to unresolved autoionization structure.

Table 1. Ammonia.

Adiabatic I.P. (eV)	Vibrational Spacing (cm^{-1})	Method*	Reference
10.176 ± 0.008	950 ± 32	This work	
10.154 ± 0.01	not assigned	PI	a
10.35	not assigned	PE	b
10.17 ± 0.01	960 (average value)	PI	c
10.15	950 (average value)	PE	d
10.175 ± 0.010	970	PE	e
10.14	968	PE	f
10.15 ± 0.02	900	PE	g

* PI denotes photoionization; PE denotes photoelectron spectroscopy.

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Fig. 2. Photoionization efficiency of O_3^+ .
(XBL 769-10672)

Table 2. Ozone.

Adiabatic I.P. (eV)	Vibrational Spacing (cm ⁻¹)	Method*	Reference
12.523 ± 0.008	650 ± 40	This work	
12.53 ± 0.01	630 (average value)	PE	a
12.52 ± 0.05	not assigned	PE	b
12.67 ± 0.02	not assigned	PI	c
12.44 ± 0.01	650 (average value)	PE	d
12.519 ± 0.004	655 ± 5	PI	e

* PI denotes photoionization; PE denotes photoelectron spectroscopy.

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* Work carried out in collaboration with Professor Johnston's and Mahan's groups.

10. PHOTOFRAGMENTATION OF BROMINE

M. J. Coggiola and P. A. Schulz

Studies have been performed recently on the photofragmentation of bromine molecules by argon ion laser light in order to better understand the fragmentation process. The angular distribution of the fragments has been measured for different wavelengths in the blue and green. The observed data were in agreement with the known dissociation energy of the $B^3\Pi$ state.

A supersonic beam of bromine was crossed with an argon ion laser in a high vacuum region. The bromine beam, seeded in argon, was collimated

using three differential pumping chambers. The polarization of the light was parallel to the axis of the molecular beam. The fragments were detected by a rotatable universal mass spectrometer.

The angular distributions have two peaks; one at zero degrees and one at an angle which is a function of wavelength. Because the transition to the B state is a parallel transition; the angular distribution peaks in the direction of the electric field (that is, at 0°). The peak at wider angles is a result of a classically infinite scattering amplitude where the velocity ray is tangent to the elastic circle. This circle is centered on the tip of the center-of-mass velocity vector and has a radius equal to the fragment recoil velocity. The fragment recoil energy is:

$$E_{\text{trans}} = M_{\text{Br}} V_{\text{cm}}^2 = h\nu - E_D$$

where ν is the frequency of the argon ion laser light and E_D is the energy of the $B^3\Pi$ continuum above the ground state of bromine.

For four wavelengths of the argon ion laser (476.5 nm, 488.0 nm, 496.5 nm, and 501.7 nm), the peak occurred in a position consistent with the dissociation energy (E_D) of 19585 cm⁻¹. For a fifth wavelength, 514.5 nm, the photon energy is not sufficient to dissociate bromine; however, a peak is observed which corresponds to the dissociation energy from $\gamma=1$ of the ground state to the continuum of the $B^3\Pi$ state.

11. CONSTRUCTION OF CHEMILUMINESCENCE-LASER FLUORESCENCE CROSSED MOLECULAR BEAM MACHINE

C. C. Kahler, Z. F. Wang, and C. H. Becker

One of the ultimate goals in kinetics is to be able to determine microscopic rate constants, the rate of reaction governing the formation of products in specific quantum states from state selected reactants. We will be able to determine in what states products are formed for various types of reactions as a function of collision energy using the recently completed chemiluminescence-laser fluorescence crossed molecular beam machine. We can cross two molecular beams (one supersonic, one effusive) at 90°. If the reaction produces products in their excited electronic state resulting in chemiluminescence, the light can be analyzed via a polychromator coupled to an optical multi-channel analyzer capable of detecting a minimum of about 100 photons/second with a signal-to-noise ratio of 2. If the reaction primarily leads to ground state products, we can investigate the branching ratios using the resonance laser fluorescence technique. A tunable laser would be focused at the collision center with the resulting fluorescence collected (by a photon counting or charge integration system) as a function of exciting wavelength. Since the crossed beams method of reaction gives us single

collision conditions, we can determine the relative populations of the product formed in each quantum state. This will also give us the highest state populated by the products giving us information on the energetics of the reaction.

We are now starting work on the series of reactions involving metastable rare gas atoms with halogen containing molecules which are important as highly efficient high power UV laser systems. We will cross xenon or krypton metastable atoms with halogen containing molecules. The Xe and Kr metastables behave much like their corresponding alkali atoms, Cs and Rb.¹ The ionization potentials are very similar and they appear to form ionic compounds readily with halogen atoms as do the alkali atoms. The reactions are believed to follow an electron jump mechanism, and therefore have large cross sections (around 200 Å²).² The system has several excited state potential curves that correlate diabatically with Xe* or Kr* (metastable ³P and high Rydberg states) + X, or low lying Xe (or Kr) + X*.³ These curves cross the Xe⁺ (or Kr⁺) + X⁻ curve at large internuclear separation (around 71 Å). As a result of the crossing, the products formed are tightly bound ionic ²Σ_{1/2}⁺ XeX* (or KrX*), which decay primarily to the repulsive or loosely bound ground state (²Σ_{1/2}⁺) giving off light in the 249-353 nm wavelength range. Monitoring this light, we'll be able to determine in what vibrational levels of the excited electronic state the products are formed. This work will help to characterize the rare gas-halide potential curves. Knowing the product state distribution will also give more information on the reaction mechanism and requirements for lasing (total gas pressure, mixture, etc.).

Another experiment we plan to do in the near future is to investigate the mechanism behind the production of chemiluminescent IF from I₂ and F₂. I₂ + F₂ → IF* has been studied in bulk reaction.⁴ Several mechanisms have been proposed but some questions still remain. Our recent investigations⁵ suggested chemiluminescent IF might exclusively come from the reaction F + I₂F → 2IF. We can cross I₂ + F₂, I + F₂, F + I₂, F + I₂F and investigate the extent of product internal excitation from chemiluminescence or probe the products by laser fluorescence. By probing the products, we will be able to determine which of the combinations give IF and which give IF* in the proper states.

12. RESEARCH PLANS FOR CALENDAR YEAR 1977

Yuan T. Lee

In early 1977, a new high resolution crossed molecular beam machine will be put into operation for the investigation of intermolecular energy transfer processes. Another new machine will also be constructed for carrying out infrared absorption spectroscopy of molecule ions in collaboration with Professor Y. R. Shen's group using a tunable IR laser.

The two new areas of reaction dynamics which we will give our major attention are reactions involving oxygen atoms which play important roles in combustion processes and chemiluminescence reactions of metastable rare gas atoms with halogen containing molecules. These reactions are responsible for the operation of a very efficient rare gas halide laser.

Works on the molecular beam photoionization studies in collaboration with Professor Mahan's group will stress on the interaction potential of ions and neutral molecules. Proton affinities are one such example. Energies of hydrogen bonding between two neutral molecules will also be investigated.

The dynamics of the multiphoton excitation and dissociation process will be investigated thoroughly. Major source of information will come from measurements of angular and velocity distributions of fragments as a function of power, pulse duration and wavelength of exciting laser. In addition to the multiphoton process, the photodissociation studies of molecules of atmospheric importance will be carried out by using the molecular beam method. Works in the general area of laser-molecule interactions will be carried out with Professor Shen's group. The works related to atmospheric chemistry will be carried out with Professor Johnston's group.

Two other areas, we expect to see some positive results, are molecular beam surface chemistry working with Professor Somorjai's group and molecular beam photoelectron spectroscopy with Professor Shirley's group.

13. 1976 PUBLICATIONS AND REPORTS

Yuan T. Lee and Associates

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h. Potential Energy Surfaces for Chemical Reactions

Henry F. Schaefer III, Principal Investigator

1. THE FUZZY INTERFACE BETWEEN SURFACE CHEMISTRY, CATALYSIS AND ORGANOMETALLIC CHEMISTRY*

Bernard R. Brooks, Charles W. Bauschlicher, Jr.,
William C. Swope and Henry F. Schaefer III

Motivated by the observation that the bonding in diatomic BeH is remarkably similar to that of transition metal hydrides, we have completed a theoretical study of chemisorption on the (0001) surface of metallic beryllium. Finite clusters as large as Be₃₆ have been used to model the metal surface, and firm conclusions drawn concerning the chemisorptive bond energies at four principle surface sites. An important result is that the chemisorptive bond energy of Be_n-H is essentially the same as the dissociation energy of diatomic Be-H. Since this same relationship has been demonstrated experimentally for the chemisorption of hydrogen on nickel surfaces, it may provide a key to the molecular understanding of surface chemistry and catalysis.

The transition metal-organic fragment bond provides a framework for such an understanding of the gray area between surface chemistry, catalysis, and organometallic chemistry. In Fig. 1, we have sketched out what is perhaps the

Fig. 1. From gas phase model systems to organo-metallic and surface chemistry. D_e values indicated are dissociation energies in kcal/mole. (XBL 771-7422)

simplest possible model relating these three disciplines. With the cooperation of the LBL Computer Center we have engaged an NRCC^T Demonstration Project on Molecular Models for Catalysis. Model systems considered to date include Mn-C₂H₂, Mn-C₂H₄, and Mn-CH₂. For the former two, one metal atom does not appear

adequate for modeling either chemisorption or organometallic π -bonding as in $\text{H}(\text{CO})_4\text{Mn}(\text{C}_2\text{H}_4)$. In this sense it seems likely that CO ligands in organometallic systems play a role analogous to that of neighboring metal atoms in surface chemistry and catalysis.

The Mn-CH₂ system does appear to serve as a reasonable model for both surface chemistry (e.g., the dissociative chemisorption of ethylene) and organometallic chemistry. Consistent with known metal-carbene complexes, the CH₂ is more strongly bound than ligands such as CO, C₂H₂, or C₂H₄. Figure 2 illustrates several potential energy

Fig. 2. MnCH₂ potential energy curves arising from manganese atom plus triplet methylene. ³B₁ CH₂ is fixed at its equilibrium geometry here, namely $r(\text{CH}) = 1.08 \text{ Å}$ $\theta(\text{HCH}) = 134^\circ$. (XBL 767-9108)

curves for the interaction of a rigid CH₂ fragment with manganese. After allowance for geometry relaxation and electron correlation, the predicted

Mn-CH₂ dissociation energy is ~ 50 kcal. The variety of different metal-carbene systems (s^2d^n or sd^{n+1} metal atom and singlet or triplet carbene ground states) is modeled by four different electronic states of the Mn-CH₂ model. The predicted CH₂ bond angles may be qualitatively understood using an extension of Walsh's rules.

* Abstracted from LBL-5474, LBL-5184, LBL-5416, and LBL-5422.

† NRCC = National Resource for Computation in Chemistry.

2. POTENTIAL ENERGY SURFACES FOR ELEMENTARY FLUORINE HYDROGEN REACTIONS*

Steven R. Ungemach and Henry F. Schaefer III

During the past decade, there has been a genuine explosion of interest in the reactions of atomic and molecular fluorine and hydrogen. As is usually the case, experimental studies have led the way, due to the tremendous impact of the HF laser. In addition to transitional kinetics, the most successful experimental techniques have been infrared chemiluminescence, chemical lasers, crossed molecular beams (in particular the work of MMRD's Dr. Y. T. Lee), and laser induced fluorescence. This experimental research has yielded a great deal of important information concerning, most of all, the $F + H_2 \rightarrow HF + H$ reaction. In addition this work has stimulated a keen interest in the detailed theoretical understanding, on the molecular level, of how this simple reaction occurs.

Somewhat more than four years ago, we reported (Science 176, 1412) an *ab initio* potential energy surface for the $F + H_2$ system. The theoretical methods used appeared to be sufficiently reliable to provide a qualitatively correct surface. Further the predicted barrier height agreed well with the experimental activation energy, as did the exothermicity.

During the past year we have been re-examining the $F + H_2$ surface with much more reliable theoretical methods. Specifically much larger basis sets (of one particle functions) and more complete configuration interaction (CI) treatments have been employed. It is well-known that in the (unattainable) limit of a complete basis set and CI expansion, one obtains the exact solution to Schrödinger's equation, and hence the exact potential surface. Although our current study is not yet completed, it is appropriate to report our preliminary results at this time. The goal of our current research is to obtain an FH₂ surface of sufficiently high reliability to be used directly (or with a very modest amount of scaling) in detailed dynamical studies.

We have been able to critically evaluate the different types of correlation effects which affect the predicted barrier height. And, in fact, the final estimated barrier, 2.7 ± 0.3 kcal, is much larger than previously expected. Careful analysis

shows that this is due to the presence of considerably less zero vibrational point energy for the saddle point than for separated $F + H_2$. Thus our prediction is consistent with the experimental activation energy of ~ 1.6 kcal. The predicted saddle point position is $r_{sp}(F-H) = 1.48$ Å, $r_{sp}(H-H) = 0.778$ Å.

* Abstracted from LBL-5482 and LBL-5779.

3. STRUCTURE, ENERGETICS, AND REACTIVITY OF CARBENES*

Charles W. Bauschlicher, Jr., Robert R. Lucchese, and Henry F. Schaefer III

Among organic species which have not been well-characterized experimentally, carbenes CR₂ are probably the most important. As such carbenes provide an excellent opportunity for fruitful theoretical research. That is, carbenes are molecules for which chemists require a better understanding, but this understanding is very difficult to come by experimentally. As a model for the reactions of carbenes with saturated hydrocarbons, we have completed a study of the $CH_2 + H_2$ reactions. Three primary conclusions may be drawn:

(a) The triplet abstraction reaction $CH_2(^3B_1) + H_2 \rightarrow CH_3 + H$ has a sizeable barrier or activation energy (~15 kcal).

(b) The Woodward-Hoffman forbidden least motion insertion reaction $CH_2(^1A_1) + H_2 \rightarrow CH_4$ has an even larger barrier (~25 kcal) associated with it.

(c) However non-least motion pathways exist (e.g., Fig. 1) which are downhill all the way,

Fig. 1. Coordinate system for the initial non-least motion approach of 1A_1 CH₂ to H₂.
(XBL 749-4316)

i.e., have no barrier at all. This is demonstrated in the contour maps of Fig. 2. These conclusions have been borne out for the $\text{CH}_2 + \text{CH}_4$

separations. These predictions are probably reliable to within a few kcal, and should provide a helpful guide to the interpretation of carbene

Fig. 2. Contour maps for the initial non-least motion approach (see Fig. 1) of singlet methylene to hydrogen. Note that R is the distance from the carbon atom to the midpoint of the H_2 bond. (XBL 766-9031)

reaction and are expected to be qualitatively correct for much larger carbene-saturated hydrocarbon reactions.

The most critical of carbene properties is ΔE , the separation between the lowest triplet and singlet electronic states. Although very crude estimates of ΔE may be attempted on the basis of carbene stereospecificity in olefin reactions, CH_2 is the only carbene for which ΔE has been determined experimentally. In Table 1 we give theoretical values for a number of singlet-triplet

reactions. For example, although chlorocarbene and bromocarbene are predicted in Table 1 to have triplet ground states, experimentalists have often concluded the opposite. In light of the greater reactivity of singlet carbenes (see above), however, it is understandable why this conclusion was drawn.

Abstracted from LBL-5194, LBL-4945, and LBL-5168.

Table 1. Mulliken populations and estimated singlet-triplet separations ΔE for several carbenes.

	Triplet C population	Singlet C population	Estimated ΔE kcal/mole
CH ₂	6.36	6.25	+19.5 ± 0.7 ^a
CHF	5.85	5.77	-2
CHCl	6.14	6.03	+6
CHBr	6.25	6.13	+8
CF ₂	5.39	5.41	-36
CCl ₂	5.99	5.89	-6

^aExperimental result of W. C. Lineberger and co-workers, J. Amer. Chem. Soc. 98, 3731 (1976).

4. THE THEORY OF SELF-CONSISTENT ELECTRON PAIRS*

Clifford E. Dykstra and Henry F. Schaefer III

The most challenging problem in electronic structure theory concerns the treatment of electron correlation in molecules. An extremely promising new approach to this problem is the theory of self-consistent electron pairs (SCEP). SCEP is unique in that pair correlation functions are expressed as (small) matrices of coefficients of products of basis functions. Through the use of an elegant operator formalism, the diagonalization of large matrices is avoided entirely. In addition the total correlation energy is rigorously expressed as a sum of variationally additive pair correlation energies.

During the past year, we have taken SCEP from formalism to a set of realistic algorithms to a reasonably efficient and operative set of computer programs. Convergence of the iterative SCEP procedure has been demonstrated for a range of molecules, including H₂, LiH, BH, Be₄, CH₂, H₂O, H₂CO, HCCCH, and C₃H₄. Several test computations for the water molecule are reported in Table 1.

Table 1. Fixed- ψ_0 SCEP studies of the water molecule.

	Energy (CI)	Energy (SCEP)	Correlation energy difference	Configurations C _{2v}	Configurations C ₁	Percentage of correlation energy Valence Total
35 basis functions						
Frozen core	-76.278910	-76.278870	0.018%	2032	7381	74.6
35 basis functions	-76.297392	-76.297354	0.015%	3238	11476	66.7
50 basis functions	...	-76.284370	...	4631	16471	75.8
Frozen core						

Note that by allowing the occupied self-consistent-field (SCF) molecular orbitals to be modified, Brueckner-like orbitals are defined which actually yield lower total energies than conventional configuration interaction (CI) including all single and double excitations. Preliminary timings indicate that the method is competitive with the most efficient CI methods in current use.

* Abstracted from J. Chem. Phys. 65, 2740 (1976), LBL-5184, and LBL-5446, and LBL-5480.

5. RESEARCH PLANS FOR CALENDAR YEAR 1977

Henry F. Schaefer III

Several studies are planned to probe more accurately the relationships between surface chemistry, catalysis, and organometallic chemistry. For example, experiments carried out during the past year have conclusively demonstrated that transition metal carbenes catalyze the olefin metathesis reaction

An accurate picture of the electronic structure of (CO)₅Cr CH₂, (CO)₅Cr CHOH (the latter a Fischer-type carbene) and certain postulated intermediates could play an important role in understanding this relatively simple system. Given adequate computational resources, we would also like to test our hypothesis (see above) that Mn₂(C₂H₄) is a reasonable model for the surface chemical bond, and explore the relationship with conventional organometallic π -complexes, e.g., H(CO)₄Mn(C₂H₄).

Despite the importance of the HCOH unit in Fischer-type transition metal carbenes M = CHOR, very little is known about this species. This lack of knowledge becomes particularly acute in light of current research in Dr. C. B. Moore's MMRD group on the laser photodissociation of

formaldehyde. Since hydroxycarbene should be a relatively stable isomer of H_2CO , its characterization may play a role in unravelling their seemingly mysterious experimental results. We plan to carry out *ab initio* studies of the potential surfaces for the triplet and singlet $\text{HCOH} \rightarrow \text{H}_2\text{CO}$ isomerization reactions. The validity of HCOH as a model for larger alkoxy-carbenes will be tested for HCOCH_3 .

A particularly important system now being investigated in Dr. B. H. Mahan's MMRD lab is the $\text{F}^+ + \text{H}_2$ reaction. Note that this reaction is as different from the neutral $\text{F} + \text{H}_2$ reaction as is night from day. While $\text{F} + \text{H}_2$ has a single potential surface of primary importance, Mahan's correlation diagram for $\text{F}^+ + \text{H}_2$ shows that one cannot possibly hope to qualitatively understand this reaction in terms of fewer than three energy surfaces. Even more important, $\text{F}^+ + \text{H}_2$ is one of the simplest chemical reactions for which electronic energy transfer is unavoidable. That is, although F^+ is readily produced in the laboratory, molecular beam studies of $\text{F}^+ + \text{H}_2$ automatically occur on excited potential surfaces since the ionization potential of F is significantly greater than that of H_2 . The goal of our research will be to fill in the missing pieces of the FH_2^+ potential surfaces. Unlike previous theoretical studies of ion-molecule reactions, we will be able to investigate several surfaces of the same symmetry, using newly developed techniques for extracting higher eigenvalues from very large secular equations.

Among several other studies planned for calendar year 1977 is a search for a fourth form of gaseous oxygen. To our knowledge, O , O_2 and O_3 (and various Van der Waal's combinations thereof) are the only species even postulated for gaseous oxygen. However the existence of S_6 as a stable molecular entity suggests O_6 as a fourth possibility. O_6 would also be isoelectronic with cyclohexane and expected to have boat and chair conformations with quite reasonable ($\sim 120^\circ$) O-O-O bond angles. Realistically we expect to find that O_6 lies energetically above 3 O_2 . Even if this is the case, it is important conceptually to understand "why S_6 and not O_6 ?" Such questions continue to be the legitimate domain of chemical theory.

6. 1976 PUBLICATIONS AND REPORTS

Henry F. Schaefer III and Associates

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Invited Lectures

1. H. F. Schaefer III, Department of Chemistry, University of California, Riverside, February 1976.
2. H. F. Schaefer III, W. F. Libby Symposium on the Relation Between Science and Technology in Heterogeneous Catalysis, UCLA, March 1976.
3. H. F. Schaefer III, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, May 1976.
4. H. F. Schaefer III, Department of Chemistry, Ohio State University, Columbus, Ohio, May 1976.
5. H. F. Schaefer III, Department of Chemistry, University of Wisconsin, Madison, July 1976.
6. H. F. Schaefer III, Department of Chemistry, University of Notre Dame, South Bend, Indiana, July 1976.
7. H. F. Schaefer III, Faraday Division (of Chemical Society) Symposium on Potential Energy Surfaces, University of Sussex, Brighton, England, September 1976.
8. H. F. Schaefer III, Oji International Symposium, Tomakomai, Hokkaido, Japan, September 1976.
9. H. F. Schaefer III, Research Institute for Catalysis, Hokkaido University, Sapporo, Japan, September 1976.
10. H. F. Schaefer III, Department of Chemistry, Kyoto University, Kyoto, Japan, September 1976.
11. H. F. Schaefer III, Department of Chemistry, Chinese University of Hong Kong, October 1976.
12. H. F. Schaefer III, Department of Chemistry, Science University, Penang, Malaysia, October 1976.
13. H. F. Schaefer III, Department of Chemistry, University of Malaya, Kuala Lumpur, Malaysia, October 1976.
14. H. F. Schaefer III, Department of Chemistry, University of Singapore, October 1976.
15. H. F. Schaefer III, Department of Chemistry, James Cook University, Townsville, Queensland, Australia, October 1976.

16. H. F. Schaefer III, Department of Chemistry, University of Queensland, Brisbane, Australia, November 1976.
17. H. F. Schaefer III, Department of Chemistry, Sydney University, Sydney, New South Wales, Australia, November 1976.
18. H. F. Schaefer III, Research School of Chemistry, Australian National University, November 1976.
19. Clifford E. Dykstra, Second International Congress of Quantum Chemistry, New Orleans, Louisiana, April 1976.
20. Clifford E. Dykstra, American Chemical Society Regional Meeting, Reno, Nevada, June 1976.
21. Clifford E. Dykstra, Department of Chemistry, University of Illinois, Urbana, Illinois, October 1976.
22. Clifford E. Dykstra, Department of Chemistry, Northwestern University, Evanston, Illinois, October 1976.
23. Clifford E. Dykstra, Bell Telephone Laboratories, Murray Hill, New Jersey, October 1976.

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3. R. R. Lucchese, and H. F. Schaefer III, Dicyanocarbene: Triplet and Singlet Structures and Energetics, *J. Am. Chem. Soc.*
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7. W. C. Swope and H. F. Schaefer III, Model Studies of π -Bonded Organometallic Systems. $Mn-C_2H_2$ and $Mn-C_2H_4$, *Molecular Physics*, LBL-5422.

8. C. E. Dykstra, An Examination of the Brueckner Condition for the Selection of Molecular Orbitals in Correlated Wavefunctions, Chem. Phys. Lett., LBL-5446.
9. C. E. Dykstra, Internal Rotation in the Ground Electronic State of Allene, J. Am. Chem. Soc., LBL-5480.
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2. ATOMIC PHYSICS

a. Low Energy Atomic Physics

Howard A. Shugart, Principal Investigator

Introduction. The atomic physics group pursues measurements which explore a number of important aspects of atomic physics and experimental techniques. During the past year significant advances have been made including: (a) The search for the influence of weak neutral currents in atomic physics progressed with the measurement of the extremely weak forbidden M1 transition probability in atomic thallium. (b) A new type of electrostatic ion trap was constructed and tested. (c) New methods employing coherent forward scattering were devised to detect trace quantities of various molecules. (d) The group hosted the 5th International Conference on Atomic Physics. These developments and others are described in the summaries and publications which follow.

1. EXPERIMENTS ON STORED IONS

Michael H. Prior, Edmond C. Wang, and Randall D. Knight

a. Electrostatic Ion Trap Development. Experimental work was initiated to verify performance predictions for ion confinement by purely electrostatic fields. The fields studied are generated by cylindrically symmetric surfaces which conform to equipotentials of the form

$$\phi(r, z) = \frac{k}{2} (z^2 - \frac{r^2}{2} + B \ln r) + C = \text{const.},$$

where r, z are cylindrical coordinates and k, B and C are constants. Positive ions with orbital angular momentum about the z -axis can be confined to a toroidal volume in which they oscillate radially and axially if $k, B > 0$. The interesting property of $\phi(r, z)$ is that the z component of ion motion is simple harmonic with frequency $\omega_z = (qk/m)^{1/2}$, where q and m are the ion charge and mass. Thus, it is possible to excite selectively ions with a particular q/m by application of a resonant oscillating electric field parallel to the z -axis. This has been accomplished in a small ion-trap constructed to approximate fields of the form given by $\phi(r, z)$. The trap, whose volume is about 50 cm^3 , easily stores 10^6 ions for about 1 second in a background pressure of about 5×10^{-8} Torr. Measurement of resonant frequencies for several ions (e.g., Ne^+ , Ar^+ , Kr^+ , Xe^+ , CO_2^+ , N_2^+) at varying potentials applied to the trap surfaces has substantially verified the predicted device behavior. An important observed phenomenon is the shift of ω_z from the predicted single ion

value by the effects of the stored ion space charge. When extrapolated to zero stored charge, measured ω_z values agree well with single ion predictions for the trap geometry used. Measurements of the decay of stored Ar^+ ions with time for various Ar atom background pressures show a collisional loss rate which is consistent with the known $\text{Ar}^+ + \text{Ar}$ charge exchange cross section. Further work is proceeding to improve the sensitivity of the ion detection scheme and to complete evaluation of the properties of this type of ion confinement device. Applications of this work may come in the areas of lifetime measurements of long-lived excited ionic states, radio-frequency spectroscopy of stored ions, and residual gas analysis.

b. $^3\text{He}^+$ 2s Hyperfine Structure. Final analysis of experimental data has been nearly completed and a value for the hyperfine structure, Δv_2 , of this metastable ion has been determined to a precision of ± 8 parts per billion. The importance of such high precision is that, when combined with the even more precisely known 1s state hyperfine structure, Δv_1 , via the quantity $D_{21} = 8\Delta v_2 - \Delta v_1$, it allows a better test of the theory of the state dependence of one electron hyperfine structure than has been available in the past. Our result produces $D_{21} = 1.189956(64) \text{ MHz}$ which differs from theory by $155(64) \text{ Hz}$. The difference between theory and experiment indicates the need for additional terms in the theory which have not yet been calculated. In particular, a quantum electrodynamic term of order $\alpha(Z\alpha)^3 \Delta v_1$ is relevant and remains uncalculated, probably because it has never before been required to reconcile theory and experiment. This work was reported at the Fifth International Conference on Atomic Physics at Berkeley, Calif., July 26-30, 1976 and is being prepared for journal publication. Consideration is being given to improvements in the experimental apparatus to allow a further increase in precision.

c. Lifetime of the $(1s2s) ^3S_1$ State of Li^+ . This helium-like ionic state is predicted by theory to decay by magnetic dipole radiation to the $1s^2 ^1S_0$ ground state with a lifetime of 49.0 sec. A curious and as yet unexplained non-exponential time dependence has been observed in the decay of this state in higher Z helium-like ions such as S^{+15} , Cl^{+16} and Ar^{+17} using the beam-foil time-of-flight technique. The question is open as to whether this peculiar behavior is some unexplained artifact of the beam-foil method or, of more interest, represents a new feature of atomic decay. We expect to determine whether Li^+ ions excited to the 3S_1 state by electron bombardment and confined inside a radio frequency

quadrupole ion trap will exhibit the same non-exponential decay. Since this approach is totally different from the beam-foil scheme, verifications of the effect would strongly argue that it is a real property of the two-electron ion. Currently, Li^+ ions are being produced from a Li atomic beam and confined inside the ion trap. The total number of stored Li^+ ions is monitored by resonant detection of their harmonic motion following pulsed excitation... a scheme quite similar to some pulsed nuclear magnetic resonance methods. At background pressures of about 1.0×10^{-8} Torr, collisions with background gas molecules produce a mean storage time of about 10 sec. With the background pressure reduced to 2×10^{-10} Torr, this should increase to about 500 sec, some 10 times the $^3\text{S}_1$ lifetime. We plan to monitor the $^3\text{S}_1$ decay by two methods: (a) via the 200 Å ML photons and (b) via the intensity of resonantly scattered laser photons tuned to excite either of the $(1s2s)^3\text{S}_1$ to $(1s2p)^3\text{P}_{0,2}$ transitions. Inasmuch as radiation from He-like ions may play an important role in diagnoses of fusion plasmas, we feel that, apart from the quite basic interest in this problem, proper interpretation of diagnostic information from these ions requires that all aspects of the decay of the $(1s2s)^3\text{S}_1$ state be understood.

2. TEST FOR PARITY VIOLATION IN NEUTRAL WEAK CURRENTS

E. Commins, S. Chu, R. Conti, D. Neuffer, and P. Bucksbaum

In this experiment, we seek to observe circular dichroism in the forbidden ML transition $6^4\text{P}_{1/2} - 7^4\text{P}_{1/2}$ (2927Å) in atomic thallium vapor ($Z=81$). As explained in last year's report, the circular dichroism effect should arise from the existence of a parity-violating neutral, weak electron-nucleon interaction predicted to exist by several gauge theories.

We have successfully completed the first state of the experiment by measuring the transition amplitude m for the ML transition: $m_{\text{Expt}} = (-2.11 \pm 0.30) \times 10^{-5} |eh/Zm_{\text{ec}}|$. This measurement constitutes S. Chu's Ph.D. thesis which has been submitted and accepted; a report of this work has also been submitted to Physics Letters. The value of m_{Expt} is in good agreement with the theoretical value obtained by D. Neuffer of our group: $m_{\text{Theory}} = -1.92 \cdot 10^{-5} |eh/Zm_{\text{ec}}|$. Neuffer has almost completed a detailed overall calculation of thallium atomic properties, the knowledge of which is necessary for prediction of the parity effect.

In the second stage of the experiment, the search for parity violation itself will be undertaken. A new and sensitive apparatus has been designed, and construction is almost complete. We will try to observe the parity-violation amplitude by detecting its interference with the "Stark" amplitude in an external electric field. Very recently, we have discovered the possibility of employing a new method which should greatly enhance the quality of the signal and suppress almost completely undesirable background effects.

3. FIFTH INTERNATIONAL CONFERENCE ON ATOMIC PHYSICS

Atomic Physics Group

R. Marrus, Conference Chairman

From July 26 through July 30, 1976, the atomic physics group hosted the Fifth International Conference on Atomic Physics. Held on the University of California, Berkeley campus, the Conference covered the most important developments in the field since the last conference two years ago and included the topics: Weak Neutral Current Effects in Atomic Physics, Tests of Quantum Electrodynamics, Exotic Atoms, High Resolution Laser Spectroscopy, Rydberg Atoms, Highly-Ionized Atoms, Electron and Atomic Collisions, and Diagnostic Problems in High Temperature Plasmas. These and other topics were covered in 32 invited talks and 223 contributed talks. A book of contributed abstracts was distributed before the conference and a collection of the invited papers will appear as a book published by Plenum Press under the title, "Atomic Physics #5."

Among the 400 participants were registrants from the following geographical areas: Brazil, Belgium, Canada, Denmark, England, Egypt, France, Germany, Ireland, Israel, Italy, Japan, Kuwait, Netherlands, Nigeria, Saudi Arabia, Scotland, Republic of South Africa, Sweden, Turkey, USA, USSR and Yugoslavia. In addition to the presentation of review and new results in the formal papers, one of the most valuable aspects of this conference is the informal personal exchange of ideas and information among participants. Open discussions with colleagues and competitors about current research is valuable in stimulating new approaches and in directing future efforts. In both the formal and informal aspects we feel the conference was highly successful.

4. ENERGY CONSERVATION AND ASTROPHYSICS

Lee Schipper

During the 1976 calendar year, I continued my work on the Coma cluster of galaxies. My first report will be submitted to a journal in December, 1976. The work involves statistics and observations of the galaxies comprising the Coma cluster. I found that the distribution of matter in the Coma cluster followed a definite elliptical pattern, rather than a spherical one as is usually assumed.

My energy related work, in conjunction with the Energy and Environment Division, continued. "Towards More Productive Energy Utilization" (LBL-3299) appeared in the Annual Review of Energy I. "Efficient Energy Use and Well-Being--The Swedish Example" (with A. Lichtenberg), LBL-4430, appeared in Science. I was made a member of the Committee on Nuclear and Alternative Energy Systems, an ERDA sponsored study run by the National Academy of Sciences. I appeared

again at the LBL summer workshop in several capacities; I presented my work at ERDA Headquarters, at the Am. Assn. for the Adv. of Science, and at several universities (U. of Chicago, MIT, Princeton, and the Royal Academy of Engineering in Sweden).

5. ATOMIC ABSORPTION SPECTROSCOPY--ATOMIC AND MOLECULAR DETECTORS

Tetsuo Hadeishi and Associates

Much of our efforts during 1976 was directed toward the optical detection of complex molecules by use of the coherent forward scattering technique. In this method, either the continuum light (D₂ lamp) or discrete lines from an electrodeless discharge lamp or tunable laser is sent through two crossed polarizer, between which is placed a cell filled with a molecular vapor. With no magnetic field, no light passes through the system. With a longitudinal magnetic field, on the molecular sample, a small part of the light (for which the plane of polarization is rotated) does pass through the system. The magnetic rotation takes place only for an electronic band system in which the molecules have a magnetic moment in at least one of the electronic states involved in the transition. The magnetic moment is large only for states with low total angular momentum. Because of this, only a few vibrational lines near the band head show the magnetic-optical rotation effect. This property results in the extreme simplification of the spectra and thus makes the identification of molecules easier. Experimental verification of this phenomenon was made for Na₂, I₂, OH and SO₂.

Other areas of work were the development of electrodeless discharge lamps for a variety of elements in high magnetic field. Both detailed theoretical and experimental studies of the interaction of radio-frequency fields with plasma discharges containing metal halide vapor were made as a function of temperature and pressure. We believe that for the first time, the usual black magic approach to lamp construction was placed on a more scientific basis. A number of stable light sources for various elements emitting intense and narrow spectra were constructed. This work is part of a RANN supported project for the development of a multiple element Zeeman atomic absorption spectrometer. With these lamps using near coincidence of some of the lines of the light source with the lines of diatomic molecules, we have made high precision measurements of absorption profile of molecules by Zeeman shifting the monitoring wavelength. This experiment was also repeated by using radiation from a frequency doubled tunable laser. The purpose of these experiments was to study the integrated absorption coefficient in order to compute the oscillator strength of the electronic transition and to obtain the pressure broadening information.

Finally, the formation of OH molecules was studied with visible and UV laser light. The OH molecules were produced by the reaction:

This reaction was studied by measuring the NO₂ with laser induced NO₂ fluorescence and by monitoring the OH molecule with tunable UV laser light which resolved the P, Q, and R electronic-vibration transitions. At elevated temperatures, N₂O₄ was decomposed to NO₂. In this case, we measured the OH concentration in the reaction

by monitoring the decrease in NO₂ concentration as well as by measuring OH fluorescence. Experiments are now underway to study the hyperfine structure and the λ doubling of OH by level crossing in a joint cooperative effort with the University of Aarhus in Denmark.

6. THEORETICAL STUDIES OF QUANTUM ELECTRODYNAMICS AND HIGH-Z IONS

Peter Mohr

I presented an invited paper entitled "Atomic Physics Tests of Quantum Electrodynamics" at the Fifth International Conference on Atomic Physics held here at Berkeley in July 1976. The paper reviews the recent developments in the comparison of theory and experiment which provide tests of quantum electrodynamics.

Work has been done on a review article (in collaboration with Stanley J. Brodsky of SLAC) on the theory of quantum electrodynamics of very strong fields. The subjects of the Lamb shift at high Z and positron production in heavy-ion collisions, which are of particular interest at LBL, are included in the article.

A study of the relativistic theory of the fine structure splitting $E(2^3P_0) - E(2^3S_1)$ in high Z helium-like ions has been made. I have evaluated the correction due to one photon exchange between the bound electrons exactly. This result together with extrapolations of the results of variational calculations at low Z, and hydrogenic Lamb shift values, provides the most accurate theoretical value presently available for the splitting. Information about this splitting is relevant to recent experiments carried out at the SuperHILAC with high-Z helium-like ions. Work is in progress on the evaluation of the self-energy contribution to the $2P_{3/2}$ state energy, in high-Z hydrogen-like systems. It is expected that the results will explain the rapid Z-dependence of the difference between theoretical and experimental values for the n=2 fine structure splitting in heavy atoms.

7. ATOMIC BEAM MAGNETIC RESONANCE

Ahsanul Huq, Atilla Ozmen, and Howard Shugart

After spending several months developing, constructing, and testing an evaporation source

for producing a beam of metastable carbon atoms, we recognized that the problems of monitoring the metastable carbon component would require more development time than was available. As a result, we turned our efforts toward a precision measurement of the ground state electronic-magnetic moment in stable lithium. This measurement was motivated by the theoretical work of Roger Hagstrom in which he compared the results using four of the best atomic lithium wavefunctions available. His results showed a variation of ~ 5 parts in 10^7 between the various computations for this parameter. It was our intention to obtain the experimental value to about 1 part in 10^7 so as to select the best of the atomic wavefunction. In order to accomplish this goal, it was necessary to perfect the method of obtaining separated oscillatory field interference patterns on magnetic field dependent resonances. This necessitates homogenizing the transition magnetic field to better than 5 parts in 10^7 over a distance of 5 inches along the beam path. In addition, it is necessary to measure or to assure accurate knowledge of the phase of the radio-frequency field at the two separated perturbation regions. We currently are refining both of these experimental requirements.

During work leading to our ultimate goal with the measurement, Atilla Ozmen has analyzed preliminary data from one hairpin resonances and obtained a value to 1 part in 10^6 which he has submitted as his doctoral thesis to the Middle East Technical University, Ankara, Turkey. His thesis title is "Precision Measurement of the Ground State g_J of Atomic Lithium." His preliminary result is $g_J(\text{Li}^7) = -2.0023002(21)$.

8. RESEARCH PLANS FOR CALENDAR YEAR 1977

Howard A. Shugart and Associates

With effectively one-half the support of previous years, the activity of the group will be reduced from 9 identifiable efforts to three principal projects. It is planned to continue the ultraviolet laser development in conjunction with the important search for the influence of weak neutral currents in atomic physics. In the ion trapping project the emphasis will be on the properties of the new electrostatic trap and on measurements of metastable lifetimes and cross sections of theoretical and practical importance. Further trace element detection studies with coherent forward scattering are planned in addition to an investigation of another possible scheme for optical separation of uranium isotopes.

9. 1976 PUBLICATIONS AND REPORTS

Howard A. Shugart and Associates

Journals

1. John F. Clauser, Experimental Investigation of a Polarization Correlation Anomaly, Phys. Rev. Lett. 36, 1223 (1976), LBL-4518.

2. A. A. Ross-Bonney, Does God Play Dice? A Discussion of Some Interpretations of Quantum Mechanics, Il Nuovo Cimento 30B, 55 (1976), LBL-3090.

3. Lee Schipper and Allan J. Lichtenberg, Efficient Energy Use and Well-Being--The Swedish Example, Science 194, No. 4269, 1001 (1976), LBL-4430, ERG-76-09.

4. R. Marrus, M. H. Prior, and H. A. Shugart, editors, "Abstracts--Fifth International Conference on Atomic Physics," July 26-30, 1976, Berkeley, California.

5. Lee Schipper, Energy Conservation: Its Nature, Hidden Benefits, and Hidden Barriers, Energy Communications, II, No. 4, 333 (1976).

6. John F. Clauser, Measurement of the Circular Polarization Correlation in Photons from an Atomic Cascade, Il Nuovo Cimento 33B, No. 2, 740 (1976), LBL-4564.

7. Lee Schipper, Toward More Productive Energy Utilization, Annual Review of Energy I (1976), LBL-3299.

Presented Papers

1. Peter J. Mohr, Atomic Physics Tests of Quantum Electrodynamics, Fifth International Conference on Atomic Physics, July 1976, LBL-5465.

2. Michael H. Prior and Edmond C. Wang, Hyperfine Structure of Stored Ions--Results for $2s\ ^3\text{He}^+$, Fifth International Conference on Atomic Physics, July 1976, LBL-5711.

3. John F. Clauser, Experiments Performed at the Lawrence Berkeley Laboratory Bearing Relation to Bell's Inequality, Thinkshops on Physics-Experimental Quantum Mechanics "Ettore Majorana," Center for Scientific Culture, Erice, Italy, April 1976, LBL-5417.

4. John F. Clauser, Philosophical Motivations of Bell's Theorem and the Experimenter's Problem, Thinkshops on Physics-Experimental Quantum Mechanics, "Ettore Majorana," Center for Scientific Culture, Erice, Italy, April 1976, LBL-5418.

5. A. A. Ross-Bonney, Classical Probability Theory from a Quantum Mechanical Viewpoint, Stanford APS meeting, Dec. 20-22, 1976.

Theses

1. Atilla Ozmen, Precision Measurement of the Ground State g_J of Atomic Lithium, (Ph.D. thesis), LBL-5718, October 1976.

2. Steven Chu, Observation of the Forbidden Magnetic Dipole Transition $6\ ^2P_{1/2} \leftrightarrow 7\ ^2P_{1/2}$ in Atomic Thallium, (Ph.D. thesis), LBL-5731, October 1976.

Reports

1. Tetsuo Hadeishi, Coherent Forward Scattering Technique for High Resolution Detection of Complex Molecules in the UV-Visible Range, Summer 1976.

2. Lee Schipper, The Swedish Experience: Saving Energy and Money, Sacramento Bee, June 1, 1976.

b. Atomic Physics

Richard Marrus, Principal Investigator

1. RADIATIVE DECAY FROM THE $2^3P_{0,2}$ LEVELS OF HELIUM-LIKE ARGON

William A. Davis and Richard Marrus

The radiative transitions $2^3P_0 \rightarrow 2^3S_1$ and $2^3P_2 \rightarrow 2^3S_1$ of helium-like argon occur in the vacuum UV at 660Å and 560Å respectively. Because these are intense lines that occur in a spectral region available to high resolution monochromators, their widths are often used for temperature determinations in high density plasmas. Measurements of the wavelengths and lifetimes are useful in checking theories of relativistic and radiative corrections to this quantity.

Using the 138.5 MeV argon beam from the LBL heavy-ion linear accelerator, the 2^3P levels of Ar^{+16} were excited by passing the beam through thin carbon foils. The resulting vacuum UV radiation was viewed downstream of the foil with a normal incidence Seya-Namioka spectrometer. Lifetime measurements were made by varying the foil position relative to the entrance slit of the monochromator. The results for the lifetimes are $\tau(2^3P_2) = 1.62 \pm .08 \times 10^{-9}$ sec and $\tau(2^3P_0) = 4.87 \pm 0.44 \times 10^{-9}$ sec. The theories can be made to agree with these results only if relativistic and quantum electrodynamic effects are taken into account. In addition, it is necessary to assume that about 50% of the 2^3P_2 decays go to the 1^1S_0 ground state by an M2 decay mode.

Precise wavelength measurements were obtained by scanning the monochromator thru the lines of interest and using synchronous data accumulation. An empirical line shape function was developed for the monochromator which takes into account the following:

- (1) Doppler shift of the emitted radiation as the beam crosses the field of view of the instrument.
- (2) Nonconstant illumination of the diffraction grating.
- (3) All nonlinear effects of the monochromator and detector. This model was tested by comparing with the known wavelengths emitted by hydrogen-like carbon and oxygen atoms produced under identical conditions to the argon lines. Good agreement was obtained.

The measured wavelengths are $(2^3P_2 - 2^3S_1) = 560.2(9)$ Å $(2^3P_0 - 2^3S_1) = 660.7(1.1)$ Å.

2. QUENCHING OF THE METASTABLE $2S_{1/2}$ STATE OF HYDROGEN-LIKE ARGON IN AN EXTERNAL ELECTRIC FIELD

H. A. Gould and R. Marrus

In this experiment, we are attempting to test the quenching theory (Bethe-Lamb theory) for the $2S_{1/2}$ state of the one-electron atom. The main interest in the theory derives from the fact that the $2S_{1/2} - 2P_{1/2}$ Lamb shift separation is an important parameter in the theory. Calculations by P. Mohr and by G. Erickson give values for this quantity which differ from each other by 2%. We believe our method can achieve an ultimate accuracy of 0.5% and distinguished between the results.

The 340 MeV argon beam is excited to the $2S_{1/2}$ level by means of a thin carbon foil. The resulting beam is then passed into a strong magnetic field. Due to the high beam velocity ($\beta = 0.1$), a motional electric field $E = \gamma\beta B$ exists in the rest frame of the ion. Stark mixing couples the metastable state with the nearby $2P_{1/2}$ state resulting in a shortened lifetime for the "mixed" state. The degree of Stark mixing depends on the Lamb shift, hence a measurement of the lifetime can be made to yield a value of this parameter.

During the last year, measurements were successfully made at 18 kG and 20 kG. The accuracy of the resultant Lamb shift value is 3%. This limit is believed to be due to detector deadtime effects. An electronic deadtime correction system has been installed, and attempts made to suppress background counts. We are now attempting to improve the accuracy of the earlier measurement.

3. LIFETIME OF THE 2^3P_0 LEVEL OF HELIUM-LIKE KRYPTON

H. A. Gould and R. Marrus

The 2^3P_0 lifetime in Kr^{+34} is sensitive to relativistic and radiative corrections. For example, the Lamb shift generates a 12% change in the theoretical lifetime. A measurement, therefore, provides a sensitive test of theories of relativistic and radiative effects.

During the last year, we succeeded in observing the decay $2^3S_1 \rightarrow 1^1S_0$ in Kr^{+34} and in measuring the lifetimes of the 2^3S_1 and 2^3P_0 levels.

III.

Nuclear Sciences

A. LOW ENERGY NUCLEAR SCIENCE

1. HEAVY ELEMENT RESEARCH

a. Actinide and Lanthanide Chemistry

Norman M. Edelstein, Neil Bartlett, John G. Conway,
Kenneth Raymond, Glenn T. Seaborg, Andrew Streit-
wiser, Jr., David H. Templeton, and Allan Zalkin,
Principal Investigators

1. HIGHLY SELECTIVE SEQUESTERING AGENTS FOR PLUTONIUM AND OTHER ACTINIDES IN THE 4+ OXIDATION STATE

a. Thorium(IV) and Uranium(IV) Complexes of Catechol

Alex A. Avdeef and Kenneth N. Raymond

The need to investigate the pathological properties of plutonium was appreciated soon after the element was produced. The hazards of potential contamination of nuclear power plant installations and personnel have been a chronic problem. The first biological studies were conducted at the University of California in 1944¹ and since then studies, including some of human subjects, have revealed some of the biological pathways of the metal.

In the living organism, it appears that plutonium is a traveling companion of iron. Ingestion of the metal into the plasma and soft tissue in animals is soon followed by the formation of a stable Pu-transferrin complex in the hepatic cells. (Transferrin is the principal iron transporting protein in the body.) Initially, only about two per cent of the metal is excreted, and most of the remainder is distributed between the skeleton (~30%, in association with stored iron and thus probably binding to phosphate ligands).² Eventually the liver receives half of the metal content in the form of long-lived insoluble deposits as a Pu-hemosiderin complex in the reticuloendothelial cells. Over a long period of time the body can retain some 80% of the original amount of the ingested plutonium.

Chemotherapeutic attempts to remove the metal have followed along traditional application of such chelating agents as EDTA. The results have not been very encouraging since such ligands also complex the trace metal ions essential to the organism and are not extremely strong sequestering agents for the actinides.

The nature of the ongoing project in this laboratory has been to design and characterize polydentate ligands that would be primarily selective for actinide(IV) ions. The biological similarities of Pu⁴⁺ and Fe³⁺ suggested that an understanding of the iron transport and storage systems would shed additional light on the nature of the plutonium retention by organisms. Ferric ion and Pu(IV) prefer similar, oxygen-containing ligands. Preliminary to the design of macrocyclic chelating agents, incorporating such ligands, that will completely enfold Pu(IV), we are determining the affinity of

the individual ligand moieties for actinide(IV) ions. One of the most promising ligands is catechol.

For the series of catechols shown below, the formation constants for the reactions (where L is the fully deprotonated

ligand) are given in Table 1. Note that the overall formation constants for the tetrakis complexes, ML₄, are as high as 10⁵⁰! The very high affinity of catechol for actinide 4+ ions gives considerable support to the design of prospective sequestering

Table 1. Stability constants for thorium catechol complexes.

Th complex	cat	tiron	ncat	dhpa
log K ₁	17.5	18.0	15.4	22.5
log K ₂	15.7	14.7	13.2	17.0
log K ₃	---	9.1	9.7	7.2
log K ₄	---	7.0	5.1	5.7
log K _{h1} ^a	---	-2.1	-3.1	-3.0
log K _{h2} ^a	---	---	-3.9	---

^aK_{hm} represent hydrolysis equilibria of the sort
ML_n(H₂O) ⇌ ML_n(OH) + H⁺; K_{hm} =
[ML_n(OH)][H] / [ML_n].

agents for Pu(IV) based on the analogous chemistry of Fe(III). Figure 1 illustrates the distribution of species in solution for the thorium nitrocatechol system as a function of pH.

Fig. 1. Distribution of species present in solution, as a function of pH, for the thorium nitrocatechol system. (XBL 7612-10902)

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b. Development of pH Titrimetric Techniques (For the Determination of Formation Constants of Actinide Complexes) Using Known Iron Catechol Systems*

Alex Avdeef, Stephen R. Sofen, Thomas L. Bregante and Kenneth N. Raymond

Catechol (1,2-dihydroxybenzene)-containing molecules are of widespread biological importance. Of prime interest to us is a class of catechol-containing molecules called the siderophores.¹ They are manufactured by enteric bacteria, such as *Escherichia coli*, for the purpose of procuring and efficiently transporting vital amounts of iron into their cells. At physiological pH iron forms a variety of polynuclear complexes of extreme low solubility. To overcome this difficulty the microorganisms are able to synthesize extremely powerful and highly selective sequestering agents. An example is enterobactin,² shown in Fig. 2.

ENTEROBACTIN

Fig. 2. Structural diagram of enterobactin. (XBL 7610-4903)

We have developed techniques for the accurate determination of the formation constants of metals with such ligands. The ligands chosen for the study have a considerable range in proton dissociation constants and include catechol (cat, 1), 4,5-dihydroxy-m-benzene-disulfonate (tiron, 2), 4-nitrocatechol (ncat, 3), 3,4-dihydroxyphenylacetic acid (dhpa, 4), and 2,3-dihydroxybenzoic acid (dhba, 5) (see preceding article 1a for the structures).

Table 2 summarizes the formation constants of the titration study. As can be seen the overall formation constant for the tris(chelate) ferric complexes range from 10^{40} to 10^{45} . Figure 3 shows the distribution of species present in the ferric

Fig. 3. Distribution of species present in solution for the ferric nitrocatechol system as a function of pH. (XBL 7612-10901)

Table 2. Stability constants for ferric catechol complexes.

Fe complex	cat	tiron	ncat	dhpa	dhba
$\log K_1^a$	20.01	20.07	17.08	20.07	20.5
$\log K_2$	14.69	14.89	13.43	14.84	7.3
$\log K_3$	9.06	9.45	9.51	9.01	4.3

$K_n = [ML_n]/[ML_{n-1}][L]$, representing $MK_{n-1} + L \rightleftharpoons ML_n$, where L = fully deprotonate ligand.

nitrocatechol system as a function of pH, which is to be compared to the corresponding one for the thorium complexes in the previous section.

* Research supported by NIH.

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c. Status Report on Macrocyclic Ligand Syntheses

Kenneth N. Raymond

Two macrocyclic ligands which we believe will be powerful chelating agents for Pu(IV) are I and II:

The preparation of the precursor tetraamine ($X = H$) had proven to be more difficult than anticipated. It has been obtained recently and higher-yield large-scale syntheses are in development.

2. SYNTHETIC AND STRUCTURAL STUDIES OF ACTINIDE AND OTHER COMPOUNDS

a. The Synthesis, Crystal Structure, and Reactions of an Actinide Metallocarborane Complex, $[U(C_2B_9H_{11})_2Cl_2]^{2-}$ *

Frank R. Fronczek, Gordon W. Hatstead and Kenneth N. Raymond

The organometallic chemistry of the lanthanides and actinides has dealt primarily with derivatives of the cyclopentadienide ion, $C_5H_5^-$, although in recent years other complexes, especially of cyclo-octatetraenide anion, have been prepared. Significant advances have now been made toward the understanding of the structure, bonding and reactivity of these compounds.¹ The (3)-1,2-dicarbollide ion, $C_2B_9H_{11}^{2-}$, has been shown to have an extensive coordination chemistry with transition metal ions, analogous to metallocenes of cyclopentadienide,²⁻⁴ but complexes of carborane ions with the f series transition metals previously have not been reported. We now have prepared, characterized and studied several key reactions of the first actinide metallocarborane complex, the anion $[U(C_2B_9H_{11})_2Cl_2]^{2-}$.

The reaction of UCl_4 with the $C_2B_9H_{11}^{2-}$ anion in tetrahydrofuran solution under inert atmosphere conditions has led to the formation of the complex anion $[U(C_2B_9H_{11})_2Cl_2]^{2-}$, which has been isolated as several air-sensitive crystalline salts. The salt $[Li(OC_4H_8)_4]_2[U(C_2B_9H_{11})_2Cl_2]$ has been subjected to an x-ray crystal structure determination using counter intensity data. The complex anion is found to exhibit approximate C_{2v} symmetry, with the ligands arranged in a distorted tetrahedral array about uranium (Fig. 1). The average U-B distance to the

Fig. 1. Atom numbering scheme and coordination-sphere distances within the $[U(C_2B_9H_{11})_2Cl_2]^{2-}$ ion. Estimated standard deviations are 0.009 Å for U-Cl, 0.03 Å for U-B, and 0.5° for Cl-U-Cl. (XBL 765-1701)

pentahapto-bonded dicarbollide ligands is 2.73(2) Å, and the average U-Cl distance is 2.599(6) Å. The Cl-U-Cl angle is $90.3(5)^\circ$, and the dicarbollide bonding face centroids form an angle of 137° about the uranium atom. The lithium cations are coordinated tetrahedrally by tetrahydrofuran molecules, with an average Li-O distance of 1.92(3) Å.

The $[C(C_2B_9H_{11})_2Cl_2]^{2-}$ anion reacts with $C_8H_8^{2-}$ to yield uranocene $U(C_8H_8)_2$, and reacts with $C_5H_5^-$ to produce products which are apparently mixed ligand complexes to dicarbollide and cyclopentadienide. Thus, in actinide complexes, the dicarbollide dianion seems to have ligating properties which are in-

intermediate between those of the cyclooctatetraene dianion and cyclopentadienide.

* Partially supported by the NSF.

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b. The Preparation, Structure Determination and Magnetic Properties of a Pyrazine-Bridged Ytterbium Cyclopentadienyl Dimer,

Edgar C. Baker and Kenneth N. Raymond

The organometallic compounds of the lanthanides and actinides have a chemistry which is distinct from either the organometallic chemistry of the d transition metals or the usual coordination chemistry of the lanthanide and actinide elements.¹ Although the magnetic properties of dimeric metal complexes can give important information about the chemical bonding, few distinct dimeric complexes of the lanthanides or actinides exist. We were

Fig. 2. A view of the pyrazine-bridged dimer, $[(C_5H_5)_3Yb \text{ N} \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array} N Yb(C_5H_5)_3]$ (XBL 7610-4954)

particularly interested in preparing such a complex in which two paramagnetic metal centers are bridged by a continuous ligand π system. The title compound is such a molecule.

The dimer was prepared from unsolvated ytterbium cyclopentadienide² and a stoichiometric amount of pyrazine in benzene and crystallized by sublimation. The structure was determined by single crystal x-ray diffraction techniques and is shown in Fig. 2.

The coordination geometry about the Yb ion is nearly C_{3v} in symmetry with three π -bonded cyclopentadienide rings disposed about the metal with an average Yb-C distance of 2.68 Å. The apical position of what may be regarded as a flattened tetrahedron is occupied by the pyrazine nitrogen with a Yb-N distance of 2.61 Å. The (center of ring) Cp-Yb-Cp angles average 118° while the Cp-Yb-N angles average 98°. The Yb-Yb distance in the dimer is 8.047 Å, which is longer than several Yb-Yb intermolecular distances in the crystal.

The long intramolecular Yb-Yb distance precludes through space magnetic interactions of the paramagnetic metal centers—hence any magnetic interaction would have to occur through interaction with the ligand π system. Magnetic susceptibility studies down to 3 K show no interaction between the two metal centers. Therefore any interaction of the 4f metal orbitals with the ligand π system (i.e., covalent bonding) must be insignificantly small.

* Partially supported by the NSF.

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c. The Structures of Dimethylhafnocene and Its Hydrolysis Product, μ -Oxo-bis(methylhafnocene) as Analogs for Organoactinides*

Frank R. Froczeck, Edgar C. Baker, Paul R. Sharp, Kenneth N. Raymond, Helmut G. Alt[†] and Marvin D. Rausch[†]

There are strong structural similarities between actinide(IV) compounds and those of zirconium and hafnium. The organometallic chemistry of hafnium has only recently begun to emerge—the first organometallic compound containing a carbon-hafnium σ -bond was reported as recently as 1971.¹ In order to obtain additional structural information on these organometallic compounds of hafnium, single crystal x-ray diffraction studies have been undertaken on dimethylhafnocene, $(\eta^5-C_5H_5)_2Hf(CH_3)_2$ (Fig. 3), and its hydrolysis product, tetra- η^5 -cyclopentadienyl- μ -oxodihafnium, $[(\eta^5-C_5H_5)_2HfCH_3]_2O$ (Fig. 4). In both compounds, the coordination geometry about hafnium is that of a distorted tetrahedron, and all cyclopentadienyl ligands are pentahapto-bonded, having essentially equivalent Hf-C distances. Dimethylhafnocene has approximate C_{2v} molecular symmetry, with an average Hf-C (methyl) distance of 2.35 Å, and an average Hf-centroid dis-

Fig. 3. Stereoscopic drawing of the dimethylhafnocene molecule. Anisotropic thermal parameters are represented by 30% probability ellipsoids. Cyclopentadienyl hydrogen atoms are represented by spheres of arbitrary radius. (XBL 757-1858)

Fig. 4. Stereoscopic drawing of μ -oxo-bis(methylhafnocene), viewed down the crystallographic two-fold axis. Thermal ellipsoids are drawn at the 25% probability level, and hydrogen atoms are omitted for clarity. (XBL 754-992)

tance of 2.210 Å. The dimeric complex has crystallographic C_2 symmetry and contains a nearly linear oxo-bridge. The Hf-O-Hf angle is $173.9(3)^\circ$, and the Hf-O distance is 1.941(3) Å. The average Hf-centroid distance in this compound is 2.225 Å, and the Hf-C(methyl) distance is 2.295(14) Å — substantially shorter than those in dimethylhafnocene.

* Partially supported by the NSF.

+ University of Massachusetts.

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d. 1,1'-Dineopentyl- and 1,1'-Di-*t*-Butoxyuranocene*

Andrew Streitwieser, Jr., Liza Sibley, and Stuart R. Berryhill

Unlike uranocene (di- π -cyclooctatetraeneuranium) and many of its derivatives, bis- π -(1,3,5,7-tetraphenylcyclooctatetraene)-uranium is remarkably air stable, perhaps because of steric hindrance to

reaction at the central metal. This result has led to a systematic study of uranocene with various numbers of different bulky groups. The neopentyl group ($(CH_3)_3CCH_2-$) is one such group. Neopentylcyclooctatetraene was prepared in 66% yield from bromocyclooctatetraene and the lithium cuprate reagent derived from neopentyl chloride. The yellow oil was characterized by pmr, cmr and mass spectra. The dianion was prepared by reaction with potassium in THF and was treated with UCl_4 to produce 1,1'-dineopentyluranocene (bis- π -(neopentylcyclooctatetraene)uranium) in 64% yield. The visible, ir, mass, pmr, and cmr¹ spectra (Table 1) are consistent with the assigned structure. The compound was air-sensitive which indicates the neopentyl groups do not supply sufficient bulk around the central metal. One reason for this is that the neopentyl group is probably in the conformation which puts the methylene protons below the plane of the cyclooctatetraene ring and the bulky *tert*-butyl group over the ring (Fig. 5) far removed from the uranium.

Table 1. Spectra of 1,1'-Dineopentyluranocene.

Proton nmr: δ 3.15 (s, 9H), methyl; -23.4 (s, 2H), methylene; -32.1 (3H), -35.4 (2H), -40.1 (2H), ring.

^{13}C nmr (relative to TMS): -17.3 ppm, methylene carbon; 36.3 ppm, methyl carbons; 74.1 ppm, quaternary carbon; 277.9 ppm, 287.9 ppm, 292.5 ppm, 304.6 ppm, 306.4 ppm, ring carbons.

Visible: λ_{max} (Nujol mull): 1360, 1312, 979, 729, 718 cm^{-1} .

Mass spectrum (m/e): 586 $(tBuCH_2C_8H_7)_2U^+$, 174 $(tBuCH_2C_8H_7)^+$, 117 $(CH_2C_8H_7)^+$, 57 $(tBu)^+$.

The proton NMR shows the chemical shift of the methylene group to be -23.5 ppm. This is considerably upfield from the chemical shift of the methylene protons of diethyluranocene (-16.3 ppm) and indicates that the methylene protons are locked in a position below the ring where they experience a

Fig. 5. Possible conformation of 1,1' dineopentyluranocene. (XBL 7612-10907)

large pseudocontact shift from the paramagnetic uranium. The calculations of the contact and pseudocontact shifts for the *tert*-butyl protons show that these protons experience some contact shift. Any rotation of the *t*-butyl group from the conformation shown in Fig. 5 would result in larger pseudocontact shifts for the methyl protons and greater disagreement with experiment.

The *t*-butoxy group is sterically similar to neopentyl but contains a conjugatively electron-donating oxygen. *t*-Butoxycyclooctatetraene² was converted to the dianion with potassium naphthalide in THF at -70°C and was treated immediately with UCl₄. The product 1,1'-di-*t*-butoxyuranocene was obtained in 77% yield after extraction into benzene. The structure is consistent with pmr, cmr,¹ visible and mass spectra (Table 2). The compound is also air sensitive undoubtedly because the *t*-butyl group is aligned away from the ring much as in Fig. 5 and provides no steric hindrance to reaction at uranium. The proton NMR is consistent with this interpretation.

Table 2. Spectra of 1,1'-Di-*t*-butoxyuranocene.

Proton nmr: δ 2.07 (s, 18H), -28.1 (s, 4H), -28.7 (s, 2H), -36.2 (s, 4H), -45.7 (s, 4H).

¹³H nmr: δ 330.0, 299.0, 296.1, 283.0, 259.6, 33.8, 1.2.

Visible: $\lambda_{\max}$ (THF) 632, 654, 680, 692.

Mass spectrum: m/e 590 (M⁺), 399, 356, 176.

* Partially supported by NSF.

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e. Bis- π -(Cyclobutenocyclooctatetraene)uranium.*

Stuart R. Berryhill and Andrew Streitwieser, Jr.

Continuing our study of novel π -ligands for actinide organometallic compounds, we report the first fused ring uraniumocene derived from cyclobutenocyclooctatetraene, **1**.

The dianion of **1** was reported by Staley, Cramer and Orvedal.¹ The dianion was prepared as the dipotassium salt, dissolved in THF and treated with UCl₄. Extraction of the crude product gave 83% of bis- π -(cyclobutenocyclooctatetraene)uranium which was further purified by sublimation at 175° and 10⁻⁶ Torr.

The compound is air-sensitive; controlled air oxidation generates **1**, an unstable hydrocarbon difficult to characterize. Spectral properties (Table 3) of the organouranium compound are consistent with the assigned structure. The proton NMR spectrum is of

Table 3. Spectra of Bis- π -(Cyclobutenocyclooctatetraene).

Proton nmr: (THF-d₈): δ -25.00 (d, 2H), endo-methylene; +19.06 (d, 2H), exo-methylene; -26.85 (s, 2H), ring; -34.44 (s, 2H), ring; -41.77 (s, 2H), ring.

Visible: $\lambda_{\max}$ 623, 651, 732 nm.

Mass spectrum: m/e 498 (M⁺, (C₁₀H₁₀)₂U⁺), 368 (C₁₀H₁₀U⁺), 340 (C₈H₈U⁺), 130 (C₁₀H₁₀⁺), 129 (C₁₀H₉⁺), 115 (C₉H₇⁺), 102 (C₈H₆⁺).

particular interest. The ring protons show a larger than usual variation but the difference between the exo and endo protons of the methylene groups of the four-membered ring are most extraordinary—the difference of 44 ppm must be the largest on record. Since the contact shifts of the two methylene protons are probably similar, the difference must result primarily from the pseudocontact shifts, an expectation borne out by calculation of the pseudocontact or dipolar contributions using assumed but reasonable geometries and magnetic moments.

* Partially supported by NSF.

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f. Syntheses, Structures and Properties of Uranium Amides.

J. G. Reynolds, A. Zalkin, D. H. Templeton, and N. M. Edelstein

We have investigated the preparation, structure, and properties of several substituted uranium (IV) amides to extend our knowledge of the chemistry of actinide elements and to look for volatile compounds of uranium which might have technical application. An earlier study¹ of U[N(C₂H₅)₂]₄ showed an unexpected dimer structure in the solid state, with a five-fold coordination which is novel for uranium (IV). Further work has now yielded several other substituted amides of uranium, and with x-ray diffraction methods we have shown them to have diverse molecular structures including a monomer,² a trimer,³ and a cyclic tetramer.⁴ A reaction with a trace of air produced a strange complex identified as [UO(C₆H₅)₂N]₃Li·O(C₂H₅)₂.² Some other new uranium and thorium amides which are liquid at room temperature and distill at temperatures below 100 K have also been prepared and identified.⁵ Spectroscopic and magnetic properties of a number of these compounds have been studied.

Uranium amides may be prepared by the direct reaction of the lithium amide with UCl_4

or by the aminolysis reaction

The compounds $\text{U}_3(\text{CH}_3\text{NCH}_2\text{CH}_2\text{NCH}_3)_6$ (trimeric in the solid state) and $\text{U}_4(\text{CH}_3\text{NCH}_2\text{CH}_2\text{NCH}_3)_8$ (a cyclic tetramer in the solid state) were synthesized by the method of Eq. 2 with N,N'-dimethylethylenediamine as the amine. The tetramer was found to be a minor product of this reaction. The monomer $\text{U}(\text{N}\phi_2)_4$ was synthesized by both reactions (1) and (2), but reaction (2) proved more useful in obtaining a pure product. The reaction of $\text{U}(\text{N}\phi_2)_4$ with a trace of O_2 and excess $\text{LiN}\phi_2$ produced the complex $[\text{UO}(\text{C}_6\text{H}_5)_2\text{N}]_3\text{Li}\cdot\text{O}(\text{C}_2\text{H}_5)_2$. The new uranium and thorium alkyl amides $\text{M}[\text{N}(\text{CH}_2\text{CH}_2\text{CH}_3)_2]_4$ and $\text{M}[\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_2]_4$, $\text{M}=\text{Th}$ and U , have been synthesized by the method of reaction (1). All these compounds are extremely air sensitive.

The trimeric compound $\text{U}_3(\text{CH}_3\text{NCH}_2\text{CH}_2\text{NCH}_3)_6$ is monoclinic, space group $\text{P}2_1/\text{a}$, with $a = 17.019(7)$, $b = 9.932(4)$, $c = 11.013(5)$ Å, $\beta = 107.45(5)^\circ$, $Z = 2$, $d_x = 2.302$ g/cm³. For 1044 reflections ($I > 3\sigma$) $R = 0.047$ and $R_w = 0.036$. The three uranium atoms, in a line, are linked with nitrogen bridges as shown in Fig. 6.

Fig. 6. Molecular structure of $\text{U}_3(\text{dmed})_6$. (XBL 763-682)

The central uranium atom has an octahedron of six nitrogen nearest neighbors at an average distance of 2.37 Å. Each terminal uranium atom is in a distorted trigonal prism of its neighbors; there are three bridge bonds and three single bonds with average distances 2.57 and 2.21 Å respectively. The rod-shaped molecules pack in the crystal in two nearly perpendicular orientations, in a manner similar to that found in the tetragonal structures of dimethylacetylene and krypton difluoride.

The tetrameric compound $\text{U}_4(\text{CH}_3\text{NCH}_2\text{CH}_2\text{NCH}_3)_8$, found as a minor product among crystals of the trimer, is orthorhombic, space group Fddd , with

$a = 12.02(1)$, $b = 22.73(2)$, $c = 34.32(3)$ Å, $Z = 8$, $d_x = 2.3$ g/cm³. For 399 reflections ($I > 2\sigma$) $R = 0.078$ and $R_w = 0.060$. Half of the nitrogen atoms act as bridges to link four uranium atoms in a nearly square configuration (Fig. 7), while the other nitrogen

Fig. 7. Structure of the cyclic tetramer, $\text{U}_4(\text{dmed})_8$. (XBL 7611-9939A)

atoms adhere each to a single uranium atom. The coordination geometry is approximately that of a trigonal prism, but with considerable distortion. In order to get acceptable refinement with the sparse data set, it was necessary to impose some assumptions on the bond distances; the final values for U-N bonds average 2.50 Å for the bridge bonds and 2.28 Å for the terminal ones.

With the bulky diphenylamido ligand, the uranium compound crystallizes as a monomer, $\text{U}[(\text{C}_6\text{H}_5)_2\text{N}]_4$; triclinic, space group $\text{P}\bar{1}$, $a = 10.74(1)$, $b = 20.22(2)$, $c = 9.86(1)$ Å, $\alpha = 92.8(1)^\circ$, $\beta = 111.0(1)^\circ$, $\gamma = 99.4(1)^\circ$, $Z = 2$, $d_x = 1.55$ g/cm³. For 1372 reflections ($I > 3\sigma$) $R = 0.050$ and $R_w = 0.049$. The molecular structure (Fig. 8) has uranium enclosed by a severely distorted tetrahedron of nitrogen atoms at an average distance 2.27 Å.

The reaction product with air, $[\text{UO}(\text{C}_6\text{H}_5)_2\text{N}]_3\text{Li}\cdot\text{O}(\text{C}_2\text{H}_5)_2$, is orthorhombic, space group Pbca , $a = 21.29(2)$, $b = 20.38(2)$, $c = 16.13(2)$ Å, $Z = 4$, $d_x = 1.59$. For 2666 reflections ($I > 3\sigma$) $R = 0.038$ and $R_w = 0.041$. The molecular structure (Fig. 9) is a dimer. The uranium atom is five-coordinate with U-N distances 2.33(1), 2.34(1), and 2.44(1) Å and bridging oxygen atoms at 2.16(1) and 2.20(1) Å. The three-coordinate lithium atom is bonded to the bridging oxygen atom at 1.93(3) Å, to the ether oxygen atom at 1.89(3) Å, and to a nitrogen atom at 2.20(3) Å.

Fig. 8. Molecular structure of $U[(C_6H_5)_2N]_4$.
(XBL 766-8198)

Fig. 9. Structure of the complex dimer,
 $[UO(C_6H_5)N]_3Li \cdot O(C_2H_5)_2]_2$. (XBL 766-8064)

g. Preparation and Structural Characterization of a New Series of Volatile Uranium Compounds, The Uranium(IV) Borohydride Etherates.

Richard R. Rietz, Norman M. Edelstein, David H. Templeton, and Allan Zalkin

Introduction. Aside from UF_6 , uranium(IV) borohydride and its methylated derivatives are the most volatile uranium compounds known.^{1,2} $U(BH_4)_4$ has been photolyzed to produce uranium atoms.³ $U(BH_4)_4$ is prepared from UF_4 and $Al(BH_4)_3$.¹ $Al(BH_4)_3$ is an explosive, oxygen and water-sensitive material. $U(BH_4)_4$ is stable for short periods in dry air, hydrolyzing over several hours, but inflames on contact with water.

Our efforts in 1976 have been threefold. First, we have studied new chemical reactions of $U(BH_4)_4$, a volatile material itself. This chemical knowledge will benefit physically oriented isotopic separation studies and may influence large scale enrichment facility design. Second, we have tried to find new routes to $U(BH_4)_4$ using readily available and safer starting materials, thus eliminating the need for $Al(BH_4)_3$. Third, we have looked for and characterized other volatile uranium borohydrides that would produce a molecular vapor from which uranium atoms might be generated.

Reactions of $U(BH_4)_4$. Uranium borohydride behaves as a Lewis acid and adds one or more molecules of a Lewis base to form addition compounds, e.g.,

	Sublimes
$U(BH_4)_4 + (CH_3)_2O \rightarrow U(BH_4)_4O(CH_3)_2$	80° C
$+ (C_2H_5)_2O \rightarrow U(BH_4)_4[O(C_2H_5)_2]_x$	50
$+ (n-C_3H_7)_2O \rightarrow U(BH_4)_4[O(n-C_3H_7)_2]_x$	70
$+ THF \rightarrow U(BH_4)_4(THF)_2$	65
$+ (CH_3)_2S \rightarrow U(BH_4)_4[S(CH_3)_2]_x$	45
$+ \text{monoglyme} \rightarrow U(BH_4)_4(\text{glyme})_x$	volatile
$+ CH_3CN \rightarrow U(BH_4)_4(NCCH_3)_x$	volatile

(x means we have not determined the number of ligands by structural analysis). All of these compounds are green crystalline solids with discrete melting points, infrared spectra, and x-ray powder patterns. As noted above, many of these materials have volatilities approaching that of $U(BH_4)_4$ itself.

When $U(BH_4)_4$ is reacted with a stronger Lewis base such as trimethyl amine, $(CH_3)_3NBH_3$ is formed and the uranium borohydride unit is destroyed.

$U(BH_4)_4[O(C_2H_5)_2]_x$. When $U(BH_4)_4$ and diethyl ether are frozen into a vessel and then warmed, the $U(BH_4)_4$ first turns from dark green to white, then dissolves to form a green solution. After the excess diethyl ether is pumped away at -78°C, a green crystalline solid remains. $U(BH_4)_4[O(C_2H_5)_2]_x$, m.p. 66°, can be slowly sublimed about a vacuum line at 20°C. It will sublime in bulk at 50°C. Its infrared spectrum indicates bonds for both uranium-hydrogen-boron units and diethyl ether.

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We have reinvestigated an observation made by Schlesinger and Brown in 1953 that one may obtain an unstable uranium borohydride etherate by the following reaction:

We have shown by physical data that this material is the same etherate as above. For a one-week reaction, followed by filtration and sublimation, the yield is 30% based on UF_4 . Thus, we now have synthesized a volatile uranium borohydride complex without using $\text{Al}(\text{BH}_4)_3$.

Our attempts to remove the ether from $\text{U}(\text{BH}_4)_4 [\text{O}(\text{C}_2\text{H}_5)_2]_x$ with BF_3 or B_2H_6 have not been successful. $\text{U}(\text{BH}_4)_4 [\text{O}(\text{C}_2\text{H}_5)_2]_x$ hydrolyzes slowly in air and inflames when in contact with water. We are studying the chemical and spectroscopic properties of this material. A crystal structure of $\text{U}(\text{BH}_4)_4 [\text{O}(\text{C}_2\text{H}_5)_2]_x$ is planned to establish the number of ligands and their modes of bonding to the uranium atom.

$\text{U}(\text{BH}_4)_4 \text{O}(\text{CH}_3)_2$. $\text{U}(\text{BH}_4)_4$ reacts with liquid dimethyl ether at -30°C to form a volatile green solid (m.p. 93°). This material sublimes at 80°C . An x-ray diffraction study on $\text{U}(\text{BH}_4)_4 \cdot \text{O}(\text{CH}_3)_2$ establishes its chemical composition. It is orthorhombic, space group Pnma , with $a = 11.423$, $b = 10.120$, and $c = 9.915 \text{ \AA}$. There are four formula units per unit cell resulting in a density of 1.99 g/cc . A total of 3277 θ - 2θ scan data, using $\text{MoK}\alpha$ x-rays, were collected, of which 1402 are unique. Each uranium atom is associated with five BH_4^- ions and one dimethyl ether molecule (see Fig. 10). The uranium

Fig. 10. Molecular structure of $\text{U}(\text{BH}_4)_4 \text{O}(\text{CH}_3)_2$ (hydrogen positions schematic). (XBL 7612-11053)

atom and one of the BH_4^- ions form a near linear chain approximately along the a axis of the unit cell (see Fig. 11). The U-B distance in the chain is

Fig. 11. Partial structure of $\text{U}(\text{BH}_4)_4 \text{O}(\text{CH}_3)_2$ showing one dimensional polymeric nature (hydrogen positions schematic). The BH_4^- units above and below the plane of the chain have been eliminated for clarity. (XBL 7612-11054)

Fig. 12. Molecular structure of $\text{U}(\text{BH}_4)_4 (\text{THF})_2$. (XBL 7612-11052)

$2.88 \text{ \AA}$, and, from similar distances found in $\text{U}(\text{BH}_4)_4$, is indicative of dihydrogen bridge bonds between the uranium and boron atoms. The other three borons are triply hydrogen bridged to the uranium atom at an average distance of $2.50 \text{ \AA}$, as is found in $\text{U}(\text{BH}_4)_4$. The U-O distance is $2.44 \text{ \AA}$. In this structure, as in the $\text{U}(\text{BH}_4)_4$ and $\text{U}(\text{BH}_4)_4 (\text{THF})_2$, the uranium is 14-coordinate, i.e., thirteen hydrogen atoms and one oxygen atom.

$\text{U}(\text{BH}_4)_4 (\text{THF})_2$. $\text{U}(\text{BH}_4)_4$ reacts with THF at room temperature to form a deep green solution. Removal

of the excess THF followed by sublimation at 60° yields a green solid (m.p. 122°). An x-ray diffraction study on $\text{U}(\text{BH}_4)_4 \cdot 2(\text{C}_4\text{H}_8\text{O})$ confirms its chemical composition. It is orthorhombic, space group Pnmc , with $a = 7.134$, $b = 11.311$, and $c = 10.442$. A total 3763 θ -2 θ scan data, using $\text{MoK}\alpha$ x-rays, were collected on a Picker FACS-I automated diffractometer, of which 915 are unique. There are four formula units in the unit cell resulting in a density of 1.74 g/cc. The coordination about uranium is approximately octahedral with four borohydride groups occupying the equatorial positions, and two oxygen atoms, from the tetrahydrofuran (THF), the apices (see Fig. 12). The U-B and U-O distances are 2.53 and 2.47 Å, respectively. The U-B distance corresponds to those previously found for triple hydrogen bridges, i.e., $\text{U} \begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{H} \end{array} \text{B}$, in $\text{U}(\text{BH}_4)_4$. The U atom is 14-coordinate with 12 hydrogen and two oxygen neighbors. Although the conventional R factor is presently 0.03, there are some disorder problems with the THF group that are yet to be resolved.

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h. Synthesis of $\text{Pa}(\text{BH}_4)_4$

R. Banks, R. Rietz, and N. Edelstein

As part of our project to study the electronic and magnetic properties of the tetravalent actinide borohydrides, we report the synthesis and identification by its x-ray powder diffraction pattern of $\text{Pa}(\text{BH}_4)_4$.

The first actinide borohydride prepared was $\text{U}(\text{BH}_4)_4$ by Schlesinger and Brown.¹ They reacted anhydrous UF_4 with an excess of $\text{Al}(\text{BH}_4)_3$ in a sealed vessel for several days at room temperature according to the reaction:

Upon pumping out the products, they obtained a dark green, air sensitive compound which is one of the most volatile of uranium, subliming in vacuum at approximately 35° with no decomposition.

In 1948, Hoekstra and Katz² synthesized the white $\text{Th}(\text{BH}_4)_4$ via a similar reaction using ThF_4 and $\text{Al}(\text{BH}_4)_3$. Being a more ionic compound, $\text{Th}(\text{BH}_4)_4$ is more stable but not nearly as volatile as the uranium analog and requires heating to 120° before it will sublime in a vacuum line.

Protactinium borohydride, $\text{Pa}(\text{BH}_4)_4$, an orange solid, was made by reacting PaF_4 and $\text{Al}(\text{BH}_4)_3$ for several days at room temperature. In the solid state, all three actinide borohydrides are isostructural.

The identity of the orange product was proven by comparing its x-ray powder pattern to that of

$\text{U}(\text{BH}_4)_4$ where the single crystal structure was solved by E. R. Bernstein, et al.³ using neutron diffraction techniques. All three borohydrides are tetragonal in the solid state belonging to the space group $\text{P4}_32_12(\text{P4}_12_12)$. Table 4 lists the lattice parameters (in Å) and calculated densities (gm-cm^{-3}) obtained from our powder patterns.

Table 4.

	a	c	c/a	ρ
$\text{Th}(\text{BH}_4)_4$	7.55±.04	13.28±.06	1.76	2.56
$\text{Pa}(\text{BH}_4)_4$	7.54±.03	13.23±.05	1.75	2.63
$\text{U}(\text{BH}_4)_4$	7.43±.04	13.17±.06	1.77	2.71

Consistent with the fact that the atomic radii decreases as atomic number increases, it is shown in the table that the lattice dimensions decrease and densities increase from Th to U while the c/a ratios assume no obvious trend.

There are six BH_4^- ions neighboring each An^{4+} ion in the crystal. Each of four are bonded through 2 An...H-B bonds and the remaining two by 3 hydrogen bridged bonds each, making the actinide ion 14 coordinate. In the gaseous state however, the uranium ion is 12 coordinate, being surrounded by a tetrahedral array of borohydride ions attached by three terminal hydrogen bridged bonds.⁴

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i. Other Crystal Structure Studies

D. H. Templeton, A. Zalkin, L. K. Templeton, G. Chapuis, A. J. Olson, N. J. Mammano, S. L. Edwards, and A. K. Cheetham

Manuscripts were completed and submitted for publication concerning several crystal structure investigation that had been started in prior years, some of them in cooperation with other LBL research groups.

A crystal of monoclinic sulfur, the form stable at normal pressure from 95°C to the melting point (and metastable at room temperature) was prepared accidentally as a by-product of synthetic work on uranium compounds. The structure refinement was carried out¹ after it was learned that the approximate structure reported by Sands² had not been refined successfully. The space group is $\text{P2}_1/\text{c}$; at 24°C $a = 10.926(2)$, $b = 10.855(2)$, $c = 10.790(3)$ Å, $\beta = 95.92(2)^\circ$, $Z = 48$ atoms, $d_x = 2.008 \text{ g/cm}^3$. For 1140 reflections ($I > 3\sigma$) $R = 0.030$. The structure (Fig. 13) is in agreement with the less precise re-

Fig. 13. Structure of monoclinic sulfur. The two alternate positions for the disordered molecules are both shown. (XBL 761-433)

sults of Sands. It contains S_8 ring molecules, and one-third of them have disorder which corresponds to a heat capacity anomaly discovered by Montgomery.³

An x-ray diffraction study⁴ of $Xe(OSeF_5)_2$ gives the first description of Xe(II) bound symmetrically to two oxygen ligands. The crystals are rhombohedral, space group $R\bar{3}m$, with hexagonal unit cell dimensions at 23.5°C; $a = 8.588(3)$, $c = 11.918(3)$ Å, $Z = 3$, $d_x = 3.345$ g/cm³. The molecules, Fig. 14,

Fig. 14. $Xe(OSeF_5)_2$ molecule as refined by least squares; three of these molecules with identical Xe and Se positions are superimposed at each site to give the disorder model. (XBL 764-1180)

lack 3-fold symmetry but lie on 3-fold axes with disorder among three orientations. The O-Xe-O configuration is linear with $Xe - O = 2.12(5)$ Å.

Two salts of the $Ni(ida)_2^{-2}$ ion ($ida = NH(CH_2COO)_2^{-2} = \text{iminodiacetate}$) were studied⁵ to aid the interpretation of rates of ligand exchange in nickel complexes measured by R. E. Connick and his coworkers. $Li_2Ni(NH(CH_2COO)_2(H_2O)_4)$ is monoclinic, space group $P2_1/n$, $a = 9.785(5)$, $b = 5.312(3)$, $c = 15.770(7)$ Å, $\beta = 99.76(5)^\circ$, $Z = 2$, $d_m = 1.67$, $d_x = 1.672$. For 1796 reflections ($I > 2\sigma$) $R = 0.031$.

$Cs_2Ni(NH(CH_2COO)_2(H_2O)_4)$ is monoclinic, space group $P2_1/c$, $a = 5.024(3)$, $b = 8.757(4)$, $c = 21.146(9)$ Å, $\beta = 96.51(5)^\circ$, $Z = 2$, $d_m = 2.31$, $d_x = 2.366$. For 2028 reflections ($I > 3\sigma$) $R = 0.024$. While the crystal structures are different, the shape and size of the nickel complex is very nearly the same in each salt. The coordination around the Ni atom (Fig. 15) is

Fig. 15. Structure of the $Ni(ida)_2^{-2}$ complex. (XBL 767-8727)

distorted from regular octahedral in ways which are the result of bond length requirements for the ligands and the crowding of some of the hydrogen atoms.

The structure of a cyclic organoplatinum (IV) complex

was studied⁶ for comparison with a related complex of Pt(II), $[Pt(CH_2)_4(PPh_3)_2]$, both of these compounds being representative of intermediates which have been postulated in catalyzed reactions of hydrocarbons. Crystals of the Pt(IV) complex are monoclinic, space group $C2/c$, $a = 15.286$, $b = 7.709$, $c = 17.036$ Å, $\beta = 107.49^\circ$, $Z = 4$, $d_x = 2.15$ g/cm³. Got 1575 reflections ($I > 3\sigma$) $R = 0.035$. The butenediyl group has disorder between two twisted conformations, one of which is shown in Fig. 16.

Crystals of an antitumor drug, 2-(3,3-dimethyl-1-triazeno)phenyl-1-carboxamide (DTPC), are monoclinic, space group $P2_1/c$, $a = 9.444(5)$, $b = 7.085(4)$,

Fig. 16. Stereogram of the molecular structure of $[\text{Pt}(\text{CH}_2)_4(\text{PMe}_2\text{Ph})_2\text{I}_2]$. Disorder occurs between right and left-handed twists of the PtC_4 ring, with the form shown here occurring about two-thirds of the time. (XBL 764-1138)

$c = 16.005(7) \text{ \AA}$, $\beta = 108.08(4)^\circ$, $Z = 4$, $d_x = 1.257$, $d_m = 1.25(1) \text{ g/cm}^3$.⁸ Its molecular structure, Fig. 17, has an internal hydrogen bond similar to that in a related derivative of triazine,⁹ and it is speculated that these hydrogen bonds may have a role in the action of this class of antitumor agents.

Fig. 17. Molecular structure of DTPC, showing the internal hydrogen bond. (XBL 757-1809)

Several derivatives of norbornane have been studied to establish the dimensions and their variation for both the framework and the attached groups to aid the interpretation of reaction rates of these compounds.¹⁰ The results are also giving data which may help establish potential energy curves for non-bonded molecular contacts which have general applicability in problems of crystal structure and molecular conformation. Crystals of sodium 2-methyl-6-

endo-hydroxybicyclo[2.2.1]heptane-2-endo-carboxylate trihydrate¹¹ are monoclinic, space group $P2_1/c$, $a = 15.887(8)$, $b = 6.459(4)$, $c = 11.829(6) \text{ \AA}$, $\beta = 106.60(5)^\circ$, $Z = 4$, $d_x = 1.406(2)$, $d_m = 1.399(7) \text{ g/cm}^3$. For 1357 reflections ($I > 3\sigma$) $R = 0.036$. The molecular structure (Fig. 18) shows a close contact between the alcohol and acid groups ($\text{C}-\text{O} = 2.783 \text{ \AA}$) and angles at C(6), C(1), and C(2) which are 5 to 7° larger than would be expected without this crowding.

Fig. 18. Molecular structure of 2-methyl-6-hydroxybicyclo[2.2.1]heptane-2-carboxylate anion. (XBL 747-1164)

Crystals of 2-exo-hydroxy-7-methylbicyclo[2.2.1]heptane-7-syn-carboxylic acid¹² are monoclinic, space group $P2_1/c$, $a = 11.58(2)$, $b = 6.874(10)$, $c = 12.02(2) \text{ \AA}$, $\beta = 115.21(5)^\circ$, $Z = 4$, $d_x = 1.306(7)$, $d_m = 1.32(1) \text{ g/cm}^3$. For 798 reflections ($I > \sigma$) $R = 0.056$. The molecular structure (Fig. 19) shows relatively little distortion resulting from the contact of alcohol and acid groups with $\text{C}-\text{O} = 2.87 \text{ \AA}$.

Fig. 19. Molecular structure of a 2,7,7-hydroxymethylacid of norbornane. (XBL 741-239)

Crystals of 6-endo-hydroxy-3-endo-aminomethyl-bicyclo[2.2.1]heptane-2-endo-carboxylic acid lactam¹³ are monoclinic, space group $P2_1/c$, $a = 10.870(3)$, $b = 7.403(2)$, $c = 10.721(4)$ Å, $\beta = 107.46(2)^\circ$, $Z = 4$, $d_x = 1.350(2)$, $d_m = 1.35(1)$ g/cm³. For 1169 reflections ($I > \sigma$) $R = 0.055$. The molecular structure (Fig. 20) shows angular distributions resulting

Fig. 20. Molecular structure of a norbornane lactam. (XBL 7611-9942)

from the close contacts of alcohol and carbonyl ($C-O = 2.832$ Å) as well as crowding of H(5) and H(10) ($H-H = 2.00$ Å). This compound was made to serve, in its rearrangement to an aminolactone, as a model for the rate determining step in the hydrolysis of amides catalyzed by chymotrypsin.¹⁴

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3. PHYSICAL AND SPECTROSCOPIC STUDIES

a. Solution Processes and Electronic Spectra for Uranium(III) and Uranium(IV) in Anhydrous Hydrogen Fluoride

M. Baluka,* N. Edelstein, and T. A. O'Donnell[†]

Introduction. Very few physico-chemical studies have been made on solutions in anhydrous hydrogen fluoride of transition metals, lanthanides, and actinides because, except for those hexafluorides which can be formed, the fluorides of these metals are sparingly soluble in the solvent.

Potentially, however, hydrogen fluoride is a very interesting solvent. It is highly acidic and has a large dielectric constant. Hence solvated cations of moderate charge should be stable in solution. Solution processes are intrinsically simpler than in water. For both solvents, simple solvation can occur and there is now some spectral evidence that coordination and crystal field effects are similar in each solvent.¹ Fluoride ligands correspond formally with hydroxide ligands but there is polarographic evidence that fluoro-complexes of cations in hydrogen fluoride are less stable than hydroxo-complexes in water.² In hydrogen fluoride there is no counterpart for oxo-complexation which leads to the formation of polymeric and other complex soluble species in water. Electrochemically, hydrogen fluoride has a very large useable potential range of about 4.5 volts with suitable electrodes.³ Therefore, voltammetry allows investigation of oxidation states for metals that are unattainable in water because oxidation of the solvent would occur. Furthermore, such HF solutions can be studied coulometrically at predetermined anodic potentials to synthesize compounds in unusually high oxidation states which could not be prepared in aqueous systems.

Dissolution of some transition metal di-fluorides and lanthanide trifluorides in HF was achieved at the University of Melbourne during 1975 by treating a suspension of the appropriate solid fluoride in HF with gaseous BF_3 at a pressure of about 2 atmospheres, and spectra of the resulting solutions were recorded.¹ Quite concentrated solutions (up to 1 M) of Ni^{2+} and Co^{2+} were obtained from difluorides within a few minutes. The trifluorides PrF_3 and NdF_3 dissolved over several hours to give relatively dilute solutions. It is postulated that the formation of BF_4 at the expense of F^- caused dissolution of the insoluble polymeric fluorine-bridged solids. BF_3 is a weak Lewis acid in the HF solvent system and it was found during 1975 that it had no discernible effect on the solubility of the tetrafluoride UF_4 in HF.

Preparation of Solution of U(IV) and U(III) in HF. Metallic uranium was treated with HF and AsF_5 . Dissolution was quite rapid and the resulting solution, green in reflected light, was red in transmitted light indicating the formation of some uranium(III). This was quite unexpected since it had previously been reported that UF_3 reduces HF and, in addition, it was expected that AsF_5 would oxidize uranium(III). Accordingly metallic uranium in HF was then treated with BF_3 , a weaker Lewis acid than AsF_5 but non-oxidizing. Within minutes, a pink color developed in the solution and this became a strong magenta color overnight. There was some apparent

formation of UF_4 . This is consistent with surface oxide on the metal providing a source of $U(IV)$, which cannot be held in solution by the weak Lewis acid BF_3 and yields a precipitate of UF_4 . Therefore, metallic uranium was treated for a short time with HF and BF_3 or AsF_5 . This procedure removed the surface contaminants and some metal and the resulting solution was poured off. There was evidence in these steps that $U(III)$ solutions in HF reacted with the surface of relatively new Kel F traps. So the remaining clean metal was treated with HF and BF_3 and the solution filtered into a Kel F trap previously treated first with ClF_3 and then with HF and H_2 . Under these conditions magenta solutions of $U(III)$ in HF were obtained which have been stable for several weeks.

Spectra of $U(III)$ and $U(IV)$ in Anhydrous HF.

Spectra were recorded on a Cary Model 17 spectrophotometer using a cell design which was a slight modification of that already reported.¹ The sample and reference cells had Kel F bodies and self-sealing synthetic sapphire windows secured by metal collars. They were filled with solution and HF respectively through Kel F valves using a small vacuum system constructed from Kel F. The cells were supported in special trays which could be located accurately in the instrument cell compartments and the trays were filled with Al_2O_3 to absorb HF in the event of accidental loss of solvent. The cell compartments were continuously purged with nitrogen.

As had been found with lanthanide spectra in HF,¹ the $U(III)$ spectrum was very similar to the aqueous solution spectrum previously reported by Cohen and Carnall⁴ who recorded their spectrum after reduction of $U(VI)$ to $U(III)$ in 1.0 M $DClO_4$ in the cell. The only major difference was that the relative intensities of the two principal bands in each solvent were reversed. The positions of the bands for each solvent are shown in Table 1.

By contrast, the $U(IV)$ spectrum in HF/ AsF_5 did not resemble the spectrum for $U(IV)$ in 1 M $DClO_4$ also recorded by Cohen and Carnall.⁴ It does however bear a very close similarity to a spectrum published by Stein and co-workers⁵ and attributed to the species UF_2^{2+} in aqueous solution. These workers had taken $U(IV)$ in 1.0 M $HClO_4$ and added HF progressively until the HF concentration in the acidic aqueous solution was 0.080 M. Figure 1a shows their spectra obtained for the following HF concentrations: A = 0.000; B = 0.020; C = 0.033; D = 0.053 and E = 0.080 M. Their initial spectrum A is very similar to that for $U(IV)$ in 1.0 M $DClO_4$ reported by Cohen and Carnall.⁴ Stein, et al. observed progressive changes with addition of HF until their spectrum E was obtained. They crystallized $UF_2SO_4 \cdot 2H_2O$ from a solution containing, initially, 6 M H_2SO_4 and 0.9 M HF.

Figure 1b gives the spectrum for $U(IV)$ in HF/ AsF_5 and, as demonstrated in Table 2, it is remarkably similar to Stein's spectrum E. It is assumed that the species UF_2^{2+} is the dominant uranium-containing species in these HF solutions.

Table 1. Spectral data for uranium(III) in water and in hydrogen fluoride.

λ (nm)	λ (nm)
$U(III)$ in 1 M $DClO_4/H_2O$	$U(III)$ in BF_3/HF
1351	1315 w.
1220	1200 vs.
1044	1070 w.
1038	1025 sh.
1035	1010 vs.
	985 sh.
996	970 w.
997	945 s.
	875 s.
898	845 vs.
876	825 vs.
727	705 m.
667	650 vw.
	640 w.
637	620 m.
615	595 vs.
547	560 s.
	520 w.
522	505 vs.
507	485 m.
451	475 m.
	445 w.
	430 m.
	410 m.

Fig. 1. Upper spectra — U^{4+} spectra obtained by Stein, et al. for the following HF concentrations: A = 0.00; B = 0.020; C = 0.033; D = 0.053; and E = 0.080 M. Lower spectrum — U^{4+} spectrum in HF/ AsF_5 . (XBL 7612-4546)

Table 2. Spectral data for uranium(IV) in water and in hydrogen fluoride.

λ (nm)	λ (nm)
U(IV) in 1 M HClO_4 /0.08 M $\text{HF}/\text{H}_2\text{O}$	U(IV) in AsF_5/HF
	1325 w.
	1295 w.
	1250 m.
1050	1040 s.
1000	1010 s.
920	930 sh.
	900 sh.
840	800 w.
770	750 m.
642	
626	600 m.
610	
590	560 w.
525	510 m.
495	
486	480 m.
469	460 m.
452	440 w.
426	420 m.
405	380 m.

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b. Optical Studies of U^{4+} in ThBr_4

M. Genet,* J. Conway, G. Shalimoff, and N. Edelstein

The work on the crystal spectra of $\text{U}^{4+}\text{-ThBr}_4$ is a joint effort of LBL and the Institut de Physique Nucléaire, Orsay, France. The Orsay group has been working with pure crystals of ThBr_4 and with ThBr_4 doped with UBr_4 . For six months of this year, Professor Michael Genet was at LBL to record the spectra of these materials. During that time a crystal growing system was set up to prepare and grow similar crystals at LBL. The system has yielded good crystals of both $\text{ThBr}_4\text{:U}^{4+}$ and $\text{LaCl}_3\text{:Nd}^{3+}$.

The spectra of $\text{U}^{4+}\text{:ThBr}_4$ crystals were recorded both on a Cary 17 spectrophotometer and photographically. The absorption spectrum from 4000 Å to 2.5

μ contains a large number of peaks. This region was observed at room temperature, liquid nitrogen and liquid helium temperatures. The Zeeman effect at liquid helium temperature was attempted but only one line exhibited any broadening at 28000 gauss and no lines were resolved. The spectrum was observed both parallel and perpendicular to the crystal axis and the lines were completely polarized.

Pure ThBr_4 fluoresces with a whitish appearance. This spectrum has been observed by the Orsay group. The $\text{U}^{4+}\text{:ThBr}_4$ also fluoresces but with a spectrum characteristic of the U^{4+} ion. The fluorescence spectra were recorded on several spectrographs at various temperatures, both with broad band excitations and with narrow band excitation in the absorption peaks.

The spectrum of $\text{U}^{4+}\text{:ThBr}_4$ contains many peaks, some very intense but many more very weak peaks. There were more peaks than expected for an f^2 electron configuration in D_{2d} symmetry. The peaks in many cases are very broad even at liquid helium temperatures, several lines are over 5 Å wide and with sharp edges. A list of absorption and fluorescence lines has been compiled.

Attempts at fitting the observed spectrum to calculations using electrostatic, spin orbit, crystal field and configuration mixing parameters is underway.

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c. Free Ion Studies of the Actinides

J. Conway and E. Worden*

Reports listing the ninety strongest emission lines of Bk and Cf in the region of 1 to 2.5 microns have been accepted for publication.^{1,2} These spectra were obtained on the Fourier transform spectrometer in Laboratoire Aime Cotton, Orsay, France.

As a follow up to the publication of the energy levels of Cm I the 2000 strongest emission lines of curium are being published.³ As a result of the isotope shift measurements done last year we have been able to greatly enlarge the shift information.

In a joint experiment between LBL, LLL, and ANL the measurements of isotope shifts in the Cf emission spectrum was undertaken. The isotopes studied are ^{252}Cf , ^{251}Cf , ^{250}Cf , and ^{249}Cf . The spectra were photographed on the 30 foot spectrograph at Argonne National Laboratory. Four different samples were made containing various mixtures of isotopes. The reduction of these data will go along with the work on the analyses of the Cf I and II spectra.

The methods of Fourier-Transform Spectroscopy (FTS) have been greatly improved in recent years. The FTS methods which first were used in the infrared are now being extended to the visible region with great success. To see if these visible instruments will be of use in our work on the actinides

some joint experiments were undertaken with the FTS group at the Kitt Peak National Observatory. As a test the emission spectra of Th and U were recorded with both an electrodeless lamp and a water cooled hollow cathode lamp as light sources. The intensity distribution vs. wavelength was calibrated using a standard lamp whose spectral irradiance is known.

The advantages of FTS are the great light gathering power of the interferometer, the wavelength calibration with only one standard line, and the accurate intensity values over a wide dynamic range. The method does require stable light sources over a long time. There remains much development work to be done on such sources.

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d. Spectra of Highly Ionized Atoms

C. Van Deurzen, T. Hayhurst, B. Lulu, and J. Conway

Vanadium 4⁺ Spectrum: V(V)

New measurements have been made with spectra taken on grazing and normal incidence spectrographs using the sliding spark as a source. The analysis has been extended to include 46 newly classified lines in the region 199 Å to 7600 Å. Five new levels in the 3p⁶ n1 configuration and two new levels in the 3p⁵ 3d4s configuration have been identified. The ionization energy is revised to 526532.0 ± 1.4 cm⁻¹ (65.2822 eV). Table 1 lists the complete set of energy levels of vanadium V.¹

The Hartree-Fock computer program of Dr. Robert Cowan of Los Alamos Scientific Laboratory is now adapted for LBL computers. In addition, Cowan's matrix element generation and energy diagonalization programs now also run on our machines. These programs generate wavefunctions and Slater parameters which serve as a starting point for the calculations of levels, spectral lines, and transition probabilities of any desired atom or ion.

The aim is to find the optimal way to use these calculations as a tool for spectroscopy. The tests are being applied to ions of the potassium isoelectronic series. The best tests are the Cr(VI) and V(V) ions. These calculations have also been made for Th(IV), U(V) and U(VI) and are proving helpful in our work on these ions.

The work on the gold spectra has started using both the sliding spark and the three electrode spark as sources. The spectrum of Au(XI) is very strong in the three electrode spark source. Much time has been spent in adjusting and calibrating the new grazing incidence spectrograph.

Table 1. Energy levels of vanadium V.

Designation	Energy (cm ⁻¹)	Interval (cm ⁻¹)	n [*]	10 ⁶ Δn [*]
3p ⁶ 4s ² S _{1/2}	148143.35		2.692624	
5s ² S _{1/2}	328217.30		3.719353	
6s ² S _{1/2}	403855.12		4.728937	
7s ² S _{1/2}	443074.72		5.733406	
8s ² S _{1/2}	466065.79		6.735789	
9s ² S _{1/2}	(480704.7) ^a			
4p ² P _{1/2}	206393.72	1266.28	2.927359	5806
2p ² P _{3/2}	207660.00		2.933166	
5p ² P _{1/2}	351500.51	517.83	3.959011	5869
2p ² P _{3/2}	352018.34		3.964881	
6p ² P _{1/2}	415420.10	255.59	4.968949	5724
2p ² P _{3/2}	415675.69		4.974674	
7p ² P _{1/2}	449586.71	186.08	5.971093	7233
2p ² P _{3/2}	449772.79		5.978326	
3d ² D _{3/2}	0.00	624.87	2.282614	1355
2d ² D _{5/2}	624.87		2.283969	
4d ² D _{3/2}	292902.86	144.38	3.434099	1066
2d ² D _{5/2}	294047.24		3.435165	
5d ² D _{3/2}	387977.07	66.62	4.449732	1070
2d ² D _{5/2}	388043.69		4.450802	
6d ² D _{3/2}	434303.77	37.15	5.453972	1098
2d ² D _{5/2}	434340.92		5.455071	
7d ² D _{3/2}	(460696.8)	(22.9)		
2d ² D _{5/2}	460719.7		6.456413	
4f ² F _{5/2}	349675.57	-423.17	3.938532	-4703
2f ² F _{7/2}	349252.40		3.933829	
5f ² F _{5/2}	417699.10	488.37	5.020705	11302
2f ² F _{7/2}	418187.47		5.032008	
6f ² F _{5/2}	449370.81	51.66	5.962733	1997
2f ² F _{7/2}	449422.47		5.964730	
7f ² F _{5/2}	469706.4	15	6.948208	892
2f ² F _{7/2}	469721		6.949101	
8f ² F _{5/2}	483019	20	7.940271	1825
2f ² F _{7/2}	483039		7.942096	
9f ² F _{5/2}	492144.3	57.5	8.931886	7476
2f ² F _{7/2}	492201.8		8.939363	
5g ² G _{7/2}	416360.29	1.49	4.990106	33
2g ² G _{7/2}	416361.78		4.990140	
6g ² F _{7/2}	450024.54	0.66	5.988154	25
2g ² G _{9/2}	450025.20		5.988179	
7g ² G _{7/2}	470333.35	0.40	6.986857	24
2g ² G _{9/2}	470333.75		6.986882	

1. C. H. H. Van Deurzen, submitted to J. Opt. Soc. Am.

Table 1 (continued)

Designation	Energy (cm ⁻¹)	Interval (cm ⁻¹)	n [*]	10 ⁶ Δn [*]
8g ² F	(483515.7)			
6h ² H°	450247.99		5.996917	
7h ² H°	470488.77		6.996539	
8h ² H°	(483626.4)			
7i ² I	470524.11		6.998746	
8i ² I	483650.82		7.998554	
9i ² I	(492651.5)			
Limit 3p ⁶ 1S ₀	526532.0			
3p ⁵ 3d ² (¹ G)				
² F _{5/2} °	319106.19	1625.41		
² F _{7/2} °	320731.60			
(¹ D) ² F _{5/2} °	337012.59	-4814.5		
² F _{7/2} °	332198.10			
(³ F) ² F _{5/2} °	396135.24	1858.42		
² F _{7/2} °	397993.66			
(³ P) ² P _{1/2} °	438018.3	1424.4		
² P _{3/2} °	439442.7			
(³ F) ² D _{3/2} °	444620.8	-467.1		
² D _{5/2} °	444153.7			
3p ⁵ 3d (³ F)4s				
² F _{5/2} °	478566	-3035		
² F _{7/2} °	475531			
(¹ F)4s ² F _{5/2} °	496296	1260		
² F _{7/2} °	497556			
(³ D)4s ² D _{3/2} °	500502	-385		
² D _{5/2} °	500117			

^aPredicted levels.

e. Spectral Properties of (Et₄N)₂UI₆ and (Et₄N)₂UF₆^{*}

W. Wagner, N. Edelstein, B. Whittaker and D. Brown

The preparation and spectral properties of octahedral compounds of the type (NEt₄)₂PaX₆ (X = F, Cl, Br, I) have recently been investigated.¹⁻³ The trends in the ligand field parameters θ and Δ for these 5f¹ complexes were explained qualitatively in terms of molecular orbital theory by large variations in σ bonding dominating the total ligand field splitting and changing markedly as the halide ion varied. This same trend was also found for salts of the hexahalogenouranates(V). As part of the above program the corresponding (NEt₄)₂UX₆ (X = F, Cl, Br, I) salts were prepared and their optical spectra obtained at 77 K.^{2,5} The most thorough analyses of

the octahedral UX₆²⁻ spectra (X = Cl, Br) have been given by Satten, Wong, et al. from data obtained at 4 K on U⁴⁺ diluted in single crystals.⁴ We report in this paper the analyses of the spectra of (NEt₄)₂UX₆ (X = I, F) and compare the trends in the parameters obtained for the U⁴⁺ series (5f²) as the halide ion is varied with the corresponding parameters in the 5f¹ series.

Fig. 2. Spectra obtained for various UX₆²⁻ (X = Cl, Br, I) compounds at ~77°K. The lines at ~1.7 μ are the (NEt₄)⁺ cation. (XBL 756-3233)

Figure 2 shows the spectra obtained for (NEt₄)₂UX₆ (X = Cl, Br, I) and for Cs₂UCl₆. As can be seen immediately the general features of these spectra are very similar, the UI₆²⁻ spectrum showing shifts to lower energies when compared to the UBr₆²⁻ and UCl₆²⁻ spectra. The situation for (NEt₄)₂UF₆ is quite different as shown in Fig. 3. This spectrum shows almost no similarity to the other UX₆²⁻ spectra and the peaks are strongly shifted to higher energies. We have assigned these spectra and obtained the "best fit" parameters shown in Table 2 and the energy levels given in Fig. 4.

Table 2. Electrostatic, spin-orbit, and crystalline field parameters for UX_6^{2-} and PaX_6^{2-} .

	UF_2^{2-a}	UCl_6^{2-a}	UBr_6^{2-a}	UI_6^{2-a}	UCl_6^{2-b}	UBr_6^{2-b}	PaF_6^{2-c}	$PaCl_6^{2-c}$	$PaBr_6^{2-c}$	PaI_6^{2-c}
$F^2(\text{cm}^{-1})$	49699 ± 465	43170 ± 2181	40867 ± 2739	38188 ± 2422	42606	41425	---	---	---	---
$\zeta(\text{cm}^{-1})$	1970 ± 10	1774 ± 35	1756 ± 41	1724 ± 39	1800	1792	1508	1523	1535	1542
$B_0^4(\text{cm}^{-1})$	10067 ± 113	7463 ± 609	6946 ± 676	6338	7211	6593	14736	6666	5413	4191
$B_0^6(\text{cm}^{-1})$	22 ± 72	992 ± 258	999 ± 252	941 ± 289	1367	1195	1423	394	-68	-282
$\Delta_{\text{rms}}(\text{cm}^{-1})^d$	67	168	176	188	---	---	---	---	---	---
$\Delta_{\text{med}}(\text{cm}^{-1})^e$	39	76	95	106	---	---	---	---	---	---

^aThis work.^bReference 4.^cReference 3.^dRoot mean square deviation.^eMean energy deviation. Fig. 3. Spectrum of $(\text{NEt}_4)_2\text{UF}_6$ at 77°K . The lines at $\sim 1.7 \mu$ are from the $(\text{NEt}_4)^+$ cation. (XBL 766-3056)

The electrostatic, spin-orbit, and crystalline field parameters obtained from our analyses and from Satten, et al.⁴ are tabulated in Table 1. One trend is immediately evident. All parameters except B_0^6 increase as the halide ion is changed from I^- to F^- . The change is most abrupt from Cl^- to F^- as expected from the spectra. The crystalline field parameters for the analogous PaX_6^{2-} and UX_6^{2-} compounds were expected to be similar, with the Pa parameters larger due to the greater magnitude of radial expectation values $\langle r^n \rangle$. The effects due to the larger radial values for Pa^{4+} would be offset to a degree by the smaller ionic radius of U^{4+} . In fact, except for the fluoride complexes, the crystalline field parameters given in Table 2 shown none of the expected trends.

The difference between the PaX_6^{2-} and UX_6^{2-} arises from the addition of a 5f electron so that in the $5f^2$ case we have the additional electrostatic parameters F^2 , F^4 , and F^6 . Our calculations were

performed with fixed ratios for F^4/F^2 and F^6/F^2 so we discuss only F^2 . One of the surprising results of our analysis is the great change in F^2 as the halide ion is varied; on the order of 20%. Let us consider only the electrostatic and spin-orbit parameters. For the PaX_6^{2-} complexes the spin-orbit parameters are approximately equal for all three compounds while for the UX_6^{2-} and the other compounds. Qualitatively, we can attribute a reduction in the spin-orbit parameter to convalency effects, which would then appear to be significant in the chloride, bromide, iodide, and PaF_6^{2-} complexes, but not in the UF_6^{2-} complex. Again, the difference between the PaF_6^{2-} complex may be attributed to the greater radial extent of the 5f wavefunction for Pa^{4+} . B. R. Judd has pointed out the observed values of F^2 for the UX_6^{2-} compounds correlate in a roughly linear way with the polarizability of the halide ion, and a qualitative calculation has shown that a nearby polarizable atom or ion will always reduce the effective coulombic interaction in a second ion. However, these qualitative models suggest larger values for the crystalline field parameters for the Pa complexes, contrary to the observed trends of the chloride, bromide, and iodide compounds.

This work shows that the parameters obtained in the usual method for analyzing optical data of 4f and 5f series may not have the same meaning for free-ion spectra and solid-state spectra. Our studies suggest the Slater parameter F^2 is strongly affected by the type of ligand in the complex and may absorb some of the effects of the ligand field. This is also true to a lesser degree for the spin-orbit coupling constant. If F^2 and ζ are affected by the ligands then the values found for the ligand field parameters may also not be the "correct" values.

Fig. 4. Energy level diagram for UX_6^{2-} ($X = F, Cl, Br, I$). The LSJ state listed for each level is the component having the largest value. (XBL 766-3039)

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f. Covalency in Octahedrally Coordinate $5f^1$ Complexes*

Norman M. Edelstein

Lanthanide compounds are generally regarded as ionic in character because the 4f electron shell

does not have a significant spatial extent and is shielded from the ligand environment by the filled $5p^{6}6s^2$ shells. The $5f$ electron shell does have a considerable spatial extent, especially at the beginning of the actinide series, and compounds of the f transition series may be characterized by covalent bonding. Experimental evidence supports this contention. The early actinide metals have properties which are more similar to d -transition series metals rather than $4f$ metals because of $5f$ electron hybridization. The stability of cyclooctatetraene complexes of the tetravalent actinide ions has been attributed to $5f$ orbital covalency. Direct evidence for covalent interactions in $5f$ compounds comes from the observation of superhyperfine structure in the electron paramagnetic resonance (epr) spectra of NpF_6 , and U^{3+} diluted in CaF_2 .

Recently we have qualitatively interpreted the magnetic resonance and optical spectra of $5f^1$ hexahalide complexes in terms of molecular orbital theory.¹ In this paper we review the application of molecular orbital theory to $5f^1$ octahedral complexes and then apply it to the data available for U^{5+} hexahalide compounds.

The energy matrices obtained from molecular orbital theory are:

$$\begin{aligned} \Gamma_7: & \begin{vmatrix} 0 & \sqrt{3} k_{a_2 t_2} \zeta \\ \sqrt{3} k_{a_2 t_2} \zeta & \Delta - \frac{1}{2} k_{t_2 t_2} \zeta \end{vmatrix} \\ \Gamma_8: & \begin{vmatrix} \Delta + \frac{1}{4} k_{t_2 t_2} \zeta & \frac{3}{4} \sqrt{5} k_{t_1 t_2} \zeta \\ \frac{3}{5} \sqrt{5} k_{t_1 t_2} \zeta & \Delta + \theta - \frac{3}{4} k_{t_1 t_1} \zeta \end{vmatrix} \\ \Gamma_6: & \begin{vmatrix} \Delta + \theta + \frac{3}{2} k_{t_1 t_1} \zeta \end{vmatrix} \end{aligned} \quad (1)$$

where the k_{ij} s are the Stevens' orbital reduction factors. For the most general case of octahedral symmetry, four orbital reduction factors are required, $k_{a_2 t_2}$, $k_{t_2 t_2}$, $k_{t_1 t_2}$, and $k_{t_2 t_1}$, where the subscripts refer to the orbital symmetries of the f electron wavefunctions. The g value for the ground Γ_7 state is

$$g_{\Gamma_7} = 2 \cos^2 \alpha - \frac{8}{\sqrt{3}} k_{a_2 t_2} \sin \alpha \cos \alpha + \frac{2}{3} (k_{t_2 t_2} - 1) \sin^2 \alpha \quad (2)$$

and for the excited Γ_7' state

$$g_{\Gamma_7'} = 2 \sin^2 \alpha + \frac{8}{\sqrt{3}} k_{a_2 t_2} \sin \alpha \cos \alpha + \frac{2}{3} (k_{t_2 t_2} - 1) \cos^2 \alpha, \quad (3)$$

and

$$\tan 2\alpha = \frac{2 \sqrt{3} k_{a_2 t_2} \zeta}{\Delta - \frac{1}{2} k_{t_2 t_2} \zeta} \quad (4)$$

One can easily show that

$$E_{\Gamma_7'} - E_{\Gamma_7} = \frac{2 \sqrt{3} k_{a_2 t_2} \zeta}{\sin 2\alpha} \quad (5)$$

When $k_{a_2 t_2} = k_{t_2 t_2} = k_{t_1 t_1} = 1$, these equations reduce to those for the ionic crystal field model.

Spectral data on NpF_6 , UX_6^- ($X = F, Cl, Br$) and PaX_6^{2-} ($X = F, Cl, Br, I$) have been published. In addition there are electron paramagnetic resonance (epr) measurements on NpF_6 , the UX_6^- compounds, and $PaCl_6^{2-}$.

Table 3 gives the results of fitting the data on the UX_6^- compounds with the crystal field model. We see that ζ is fairly constant for all three complexes but Δ , which depends only on π bonding, decreases markedly as the ligand changes from F^- to Br^- .

Table 3. Values of ζ and Δ obtained from crystal field theory.

Compound	g_{exp}^a	$E_{\Gamma_7' - \Gamma_7}$ (cm^{-1})	ζ (cm^{-1})	Δ (cm^{-1})
UF_6^-	-.748	7413	1970	3882
UCl_6^-	(-)1.12	6801	1938	2056
UBr_6^-	(-)1.21	6823	1961	1623

^a Parentheses indicate the sign of the g value is not measured.

Now let us consider the same data but apply the molecular orbital theory. In this case we use the free ion value of ζ which has been calculated from relativistic wavefunctions to be $\zeta = 2172 \text{ cm}^{-1}$ for U^{5+} , and by comparison with the available experimental data has been estimated to be accurate to $\pm 50 \text{ cm}^{-1}$. From Eqs. 2, 4, and 5 we can evaluate the three parameters, $k_{a_2 t_2}$, $k_{t_2 t_2}$, and Δ_0 . The approximation $k_{a_2 t_2} = \sqrt{k_{t_2 t_2}}$ was made by Eisenstein and Pryce and by Hecht, et al.^{2,3} We make the same approximation and note from Eq. 5 that

$$\sin 2\alpha = \frac{2 \sqrt{3} k_{a_2 t_2} \zeta}{E_{\Gamma_7'} - E_{\Gamma_7}} \leq 1. \quad (6)$$

The results are given in Table 4.

Table 4. Values of $k_{t_2 t_2}$ with the approximation

$$k_{a_2 t_2} = \sqrt{k_{t_2 t_2}}, \quad \zeta = 2172 \text{ cm}^{-1}.$$

Compound	$\Gamma_7' - \Gamma_7$ (cm^{-1})	g_{exp}	g_{calc}	$k_{t_2 t_2}$
UF_6^-	7413	-.748	-.747	.870
UCl_6^-	6801	(-)1.12	---	---
UBr_6^-	6823	(-)1.21	---	---

With the experimental data, the calculated free ion spin-orbit coupling constant ζ , and the above approximation, it is impossible to fit the experimental data for UCl_6^{2-} and UBr_6^{2-} . We conclude the approximation $k_{a_2 t_2} = \sqrt{k_{t_2 t_2}}$ is not valid.

The next step is to allow k_{a2t2} and k_{t2t2} to be independent. However, we do not have enough experimental data to unambiguously fit k_{a2t2} and k_{t2t2} for each of the three complexes. We assume that k_{a2t2} and k_{t2t2} will be close to 1 and find the maximum values for each parameter which will fit the experimental data. This procedure at the very least will provide the trends in the orbital reduction factors as the halide is varied. The results are shown in Table 5.

Table 5. Maximum values of k_{a2t2} and k_{t2t2} obtained with $\zeta = 2172 \text{ cm}^{-1}$.

Compound	$E_{\Gamma_7-\Gamma_7'}$ (cm^{-1})	g_{exp}	g_{calc}	k_{a2t2}	k_{t2t2}	$\Delta \text{ calc}$ (cm^{-1})
UF_6^-	7413	-.748	-.745	.935	.95	3369
UCl_6^-	6801	(-)1.12	-1.12	.903	.75	1119
UBr_6^-	6823	(-)1.21	-1.21	.906	.50	835

First of all, we are able to fit the data for the three UX_6^- complexes with this model. Secondly, the value of k_{a2t2} appears almost constant for the three complexes although k_{t2t2} changes markedly. However, small changes in the value of k_{a2t2} . Qualitatively, the results follow the expected pattern. The orbital reduction factors are smaller (more covalent bonding) for the less electro-negative ligands, i.e., the $\text{U}^{5+} - \text{Br}^-$ bond is more covalent than the $\text{U}^{5+} - \text{F}^-$ bond. Thirdly, the value of the ligand field parameter Δ is strongly affected by the values of k_{a2t2} and k_{t2t2} ; for the UCl_6^- and UBr_6^- complexes this parameter is approximately half the magnitude as found with the crystal field theory.

Finally, we wish to point out that the values of k_{a2t2} and k_{t2t2} can be determined unambiguously. Equation 3 shows the g value for the excited Γ_7' state which also depends on k_{a2t2} and k_{t2t2} . The measurement of this quantity will allow us to unambiguously determine the orbital reduction factors. Table 6 shows the calculated values of $g_{\Gamma_7'}$ for the UX_6^- complexes based on the data previously given for the crystal field model and the molecular orbital model. Essentially the deviations of the sum of g_{Γ_7} and $g_{\Gamma_7'}$ will be due to the orbital reduction factors.

Table 6. Calculated values of $g_{\Gamma_7'}$ using the crystal field model the molecular orbital theory.

Compound	$g_{\Gamma_7 \text{ exp}}$	C.F. $g_{\Gamma_7' \text{ calc}}$	M.O. $g_{\Gamma_7' \text{ calc}}$
UF_6^-	.748	2.748	2.72
UCl_6^-	-1.12	3.12	2.95
UBr_6^-	-1.21	3.21	2.88

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4. RESEARCH PLANS FOR CALENDAR YEAR 1977

Norman M. Edelstein, Neil Bartlett, John G. Conway, Kenneth Raymond, Glenn T. Seaborg, Andrew Streitwieser, Jr., David H. Templeton, and Allan Zalkin

The basic purpose of this project is to study lanthanide and actinide materials in order to provide the basic knowledge necessary for their safe and economic utilization in present and future technology. This work encompasses related problems of an applied nature in actinide chemistry.

This program includes the preparation of new gaseous, liquid, and solid phases, and studies of their physical and chemical properties. Techniques utilized for characterization include x-ray diffraction, optical and vibrational spectroscopy, magnetic resonance, and magnetic susceptibility. Equilibrium and kinetic data for complex formation will be measured. From these complementary studies, new insights into the structural and chemical principles of actinide compounds will be obtained with which to design new synthetic schemes to produce new materials.

A major aspect of our program is the design of sequestering agents for actinide ions which can engulf the ion and generate neutral or negatively charged complexes. The sequestering agents will have a very high specificity for actinide ions as well as large absolute formation constants with these ions. Such compounds may have use in the treatment of actinide poisoning or in new processing schemes for nuclear waste. A systematic application of various macrocyclic polydentate chelating agents containing such functional groups as hydroxamate and catecholate anions to the lower oxidation state actinide ions will be investigated. Reagents will be developed which can be used to extract the actinides from aqueous media.

The preparation of new organoactinide compounds and their characterization is of great chemical and perhaps industrial importance. The discovery of uranocene by Streitwieser and Müller-Westerhoff in 1968 has led to a renaissance of interest in actinide organometallic compounds. Work in progress includes a study of related di- π -cyclooctatetraene-thorium compounds, ligand equilibria of substituted uranocenes, uranocenes with sterically hindering *t*-butyl groups and organoactinide compounds with other π -ligands such as *s*- and *as*-indacene, 2,2'-bi-indenyl and [16]annulene. Studies will be extended to higher *Z* actinides. The preparation and characterization of new organoactinide and lanthanide complexes which 1) contain carborane anions or 2) are dimeric species linked by π ligand systems will continue.

The preparation and physical studies of new actinide amide, alkoxide, and borohydride compounds

will continue. The characterization of actinide ions in anhydrous hydrogen fluoride will be extended to Np and Pu and electrochemical studies on these ions will be carried out in this solvent. The investigation of new methods for the synthesis of simple $UF_xX_{(6-x)}$ or $UF_xX_{(4-x)}$ species will proceed. The high electronegativity of the U ion requires that X should also be an electronegative ligand. Possible ligands are OF, OCF_3 , OSO_2F , OSF_5 . The first is the most attractive for application to isotope separation. It is also of fundamental interest since no fluoroxy compound of a transition element has even been prepared, although a number of fluoroxy compounds have been derived from the non-transition elements (e.g., $FOCF_3$, $(FO)_2CF_2$, $FONO_2$, $FOSF_5$). The spectroscopic program will emphasize the crystal spectra of tetravalent actinide ions in the host crystal $ThBr_4$ and the interpretation of the data. The analysis of the spectrum of Cf will be extended. The study of the spectra of highly ionized atoms will be carried out with the SuperHILAC as a source. In addition, a program to utilize the injector beam research facilities as a source of highly ionized atoms will be initiated.

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* Partially supported by the NSF.

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Invited Lectures

Andrew Streiweiser

"Uranocene - an f-Orbital Organometallic Sandwich Compound" given as follows:

Feb. 10, 1976	[†] University of Tübingen, West Germany
Feb. 16	[†] University of Karlsruhe, West Germany
April 7	Kernforschungszentrum Karlsruhe, West Germany
April 9	[†] Phillips University, Marburg, West Germany
April 26	University of Göttingen, West Germany
May 6	[†] Erlangen-Nürnberg University, West Germany
May 18	Greek Atomic Energy Commission Laboratory, "Demokritos", Athens

May 31	Max Planck Institute, Mülheim, West Germany	June 4	[†] University of München, West Germany
June 1	[†] University of Heidelberg, West Germany	June 18	E.T. H., Zürich, Switzerland
June 2	University of Stuttgart, West Germany	<hr/> [*] Partially supported by the NSF. [†] Talk given in German.	

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IV.

Advanced Isotope Separation Technology

1. LASER CONCEPTS

a. Molecular Beam Laser Isotope Separation

Y. T. Lee and Y. Ron Shen, Principal Investigators

Introduction. The purpose of this program is two-fold. By using the molecular beams method, we hope to investigate basic physical and chemical processes which play important roles in various established isotope separation processes. And by taking advantage of both the molecular beams method and laser technology, we hope to develop new concepts and new methods for efficient separation of isotopes.

Three methods which we are investigating using molecular beam laser isotope separation schemes are:

- (1) Selective decomposition of van der Waal's molecule-recoil separation through vibrational relaxation.
- (2) Selective condensation through modification of sticking coefficients.
- (3) Molecular beam studies of multiphoton dissociations.

Extensive investigations have been made during the past year in the formation of van der Waals molecules, the relaxation of vibrationally excited molecular complexes and on multiphoton dissociation processes.

1. PHOTOIONIZATION OF RARE GAS VAN DER WAALS MOLECULES

P. W. Tiedemann and C. Y. Ng

The photoionization efficiency curve for a rare gas van der Waals molecule yields in principle information about the potential energy curve of the corresponding ion-atom pair and the photoionization mechanism. Such information has recently become of much interest, as UV lasers have been suggested based on transitions from excited levels of rare gas dimer molecules to the ground state.¹ One means of obtaining the dissociation energy of diatomic rare gas ions is through photoionization in a high pressure gas cell;² however, the dimeric ions are produced by an associative ionization process and thus only a lower bound on the dissociation energy of the ground ionic state is provided. Another way of obtaining the interaction potentials is by studying the low energy differential elastic scattering of the rare gas ions on the corresponding atoms.³

We report here the direct photoionization of the asymmetric rare gas diatomic van der Waals molecules XeKr, XeAr and KrAr. The symmetric molecules have been studied previously.^{4,5}

The molecules of interest are produced in the adiabatic expansion of appropriate mixtures of the rare gases through a 0.127 mm diameter nozzle. It is important to premix the rare gases in adequate proportions, so as to maximize formation of the asymmetric diatomic molecule; of course, the symmetric diatomic molecules compete in the formation process and collisions in the expanding supersonic beam as well as the relative well depths of all the possible molecules which can be formed play a role. Figure 1 shows the experimental photoionization curve of KrAr as a function of the Kr-Ar ratio. (This ratio has been obtained by photoionization and has been corrected for the relative ionization cross sections.) Similar curves have been obtained for XeKr and XeAr.

In the apparatus^{4,5} used in these experiments the supersonic beam is intercepted by a monochromatic vacuum ultraviolet photon beam, produced either in a pulsed helium discharge lamp (helium Hopfield continuum) or a hydrogen-deuterium discharge lamp (hydrogen many line pseudo-continuum). The ions formed are mass analyzed in a quadrupole spectrometer and detected using a pulse counting technique.

Fig. 1. Photoionization curve of KrAr.
(XBL 7612-10879)

Fig. 2. Photoionization curve of XeAr. (XBL 7612-10877)

Figure 2 shows the photoionization efficiency curve for the XeAr molecule. From the threshold value of 1036 Å along with the ionization potential of xenon and the binding energy of neutral XeAr, obtained from elastic scattering experiments,⁶ the well depth for XeAr⁺ is calculated as 0.14 eV. In the same way for XeKr⁺ and KrAr⁺ the well depths are 0.37 eV and 0.59 eV, respectively. These values do not compare well with calculated ion-induced dipole interaction energies, except for the XeKr⁺ case, where the attractive energy between Xe⁺ and Kr is 0.34 eV. This indicates as expected, that the ion-induced dipole picture is not a good one, when an ion far from being a point charge interacts with an atom of rather low polarizability.

From the onset until 900 Å the spectrum in Fig. 2 is basically identical to the xenon photoionization efficiency curve, except for the threshold behavior and that all peaks experience a red shift of 3 Å. Below 900 Å the spectrum consists of a series of peaks which correlate well with argon atomic lines. This entire structure is consistent with XeAr molecules being first excited and then autoionizing into the levels of the molecular ion XeAr⁺. The shift in the peak positions corresponds to the difference in the well depth of the ground-state molecule and the potential of an electronically excited molecule at the van der Waals radius of the ground state molecule; this difference is 0.04 eV for XeAr.

The KrAr spectrum is almost identical to the XeAr spectrum in the 890-800 Å region, except for a slight shift in the peak positions, once more providing evidence that these peaks are due to argon; the krypton features are less

distinct however. The XeAr spectrum is rendered less clear because of overlap of xenon and krypton lines; in spite of this all lines could be assigned.

Due to the high sensitivity of the present beam apparatus these experiments provide considerable information which cannot be obtained as easily with other techniques.

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2. THE BINDING ENERGY AND THE RELAXATION OF NO-NO⁺

C. Y. Ng and P. W. Tiedemann

In this work, we report the first photoionization study of (NO)₂.¹ One of the reasons for this study was to determine the binding energy between NO and NO⁺. The other is to demonstrate the efficiency of vibrational to translational and rotational relaxation which leads to dissociation

Fig. 1. Photoionization spectrum of $(\text{NO})_2$. (XBL 7611-9943)

of complex ions. If the ionization mechanism of $(\text{NO})_2$ is such that only one of the NO molecules in the dimer is being excited to the different vibrational states of $\text{NO}^+(\text{X}^1\Sigma^+)$, we would expect to see the same step-function behavior that is observed in the photoionization efficiency curve of NO alone.² Furthermore, since the intermolecular energy transfer in the $\text{NO}-\text{NO}^+(\text{X}^1\Sigma^+)$ complex is expected to be faster than the ion transit time to the detector ($\sim 10^{-6}$ sec), if the energy of a certain vibrational level of $\text{NO}^+(\text{X}^1\Sigma^+)$ is greater than the binding energy of $\text{NO}-\text{NO}^+$, the complex will no longer be stable. Thus the number of steps observed in the photoionization efficiency curve will be related to the binding energy of $\text{NO}-\text{NO}^+(\text{X}^1\Sigma^+)$.

The photoion yield spectrum of $(\text{NO})_2$ obtained is shown in Fig. 1. The photoionization efficiency curve (P.E.) of NO is also plotted for comparison. The ionization potential obtained in this work is equal to 8.746 ± 0.015 eV. From this, and the dissociation energy of $(\text{NO})_2$ (0.069 ± 0.004 eV) obtained by Billingsley and Callear,³ the dissociation energy of $\text{NO}(\text{X}^1\Sigma^+, v''=0) - \text{NO}^+(\text{X}^1\Sigma^+, v'=0)$ is deduced to be 0.587 ± 0.015 eV. However, in the photoion yield curve of $(\text{NO})_2$, only two steps are clearly resolved. They are separated by 0.29 eV, which is the vibrational quantum of the NO molecule. In order to rationalize the observed features in the P.E. curve of $(\text{NO})_2$, schematic representations of the potential energy curves for $(\text{NO})_2$ and $(\text{NO})_2^+$ are shown in Fig. 2. The quantities ϵ and ϵ^+ are the dissociation energies of $\text{NO}-\text{NO}$ and $\text{NO}-\text{NO}^+$ respectively. The ionization process of $(\text{NO})_2$ involves ejecting an antibonding electron which is associated with one of the NO molecules. This results in the excitation of the stretching mode of NO^+ . The onset of the first step in the P.E. curve [i.e., I.P. of $(\text{NO})_2$] can be attributed to

Fig. 2. Schematic representation of $\text{NO}+\text{NO}$ and $\text{NO}+\text{NO}^+$ potential energy curves. ϵ^+ and ϵ denote the dissociation energies of $(\text{NO})_2^+$ and $(\text{NO})_2$ respectively. (XBL 767-8665)

the ionization threshold of $(\text{NO})_2$ to form $\text{NO}-\text{NO}^+(v'=0)$. The onset of the second step is then equal to the I.P. of $(\text{NO})_2$ to form $\text{NO}-\text{NO}^+(v'=1)$.

With this model, the nonexistence of the third step in the P.E. curve suggests the NO-NO^+ ($v'=2$) has an energy larger than the ion-neutral bonding energy. Thus we have

The fact that NO-NO^+ ($v'=1$) is bound but NO-NO^+ ($v'=2$) is not, as suggested by the P.E. curve, also permits a measurement of the well depth of NO-NO^+ . Thus the minimum well depth for NO-NO^+ ($v'=0$) is 0.29 ± 0.015 eV and the maximum is estimated to be 0.58 ± 0.015 eV (ϵ_{max}^+) which correspond to the vibrational energies of NO^+ ($v'=1$) and NO^+ ($v'=2$) respectively. From Fig. 2, the following relation can be derived.

$$\epsilon^+ + \text{I.P.}(\text{NO})_2 = \text{I.P.}(\text{NO}) + \epsilon. \quad (1)$$

Using ϵ_{max}^+ and substituting in Eq. (1), an upper bound for the dissociation energy of $(\text{NO})_2$ is found to be 0.062 ± 0.015 eV. Although this method cannot serve to measure the dissociation energy of $(\text{NO})_2^+$ to better than one vibrational quantum, these values certainly lie within the estimates derived by the thermochemical cycle.

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3. A MOLECULAR BEAM STUDY OF MULTIPHOTON DISSOCIATION OF SF_6

M. J. Coggiola, P. A. Schulz, and E. R. Grant

A crossed molecular beam apparatus has been adapted to study the dissociation of polyatomic molecules in intense IR laser fields. Initial experiments have involved the study of the dissociation of SF_6 by CO_2 laser radiation at $10.6 \mu\text{m}$. A molecular beam of SF_6 was formed by supersonic expansion using three stages of differential pumping. A grating tuned pulsed CO_2 TEA laser was used as the excitation source. The laser beam was focused by a 25 cm f.l. ZnSe lens, and crossed the molecular beam near its focal point. The fragments produced by multiphoton dissociation of SF_6 within the small interaction region were detected as a function of recoil angle and velocity.

Figure 1a shows the measured angular distribution of four species, SF_5^+ , SF_4^+ , SF_3^+ , and F^+ . The average power density used was $5 \times 10^8 \text{ W/cm}^2$. The angular distribution of a particular fragment is a very sensitive function of its mass and recoil velocity, and thus the invariance of the fragment angular distributions shown clearly implies that they all are due to the same parent, SF_5 . This result then unambiguously identifies the primary dissociation products at this power

density as SF_5 and F . Figure 1b shows a kinematic diagram of the present experiment. The concentric circles centered on the tip of the SF_6 velocity vector (V) represent the locus of center-of-mass recoil velocities that an SF_5 fragment can have for a given amount of released translational energy. The maximum laboratory scattering angle for a particular energy can be found on this diagram as the angle between V and the laboratory SF_5 velocity vector (V') that is tangent to the appropriate circle. Since the majority of SF_5 fragments were detected with 20° of the beam, the average energy released into translation is less than 1.5 kcal/mole.

A more detailed profile of the SF_5 fragment recoil energy distribution has been obtained from a kinematic analysis of the angular distribution together with time-of-flight velocity measurements. Relative probabilities taken from the normalized distribution have been listed in Table 1. An RRKM theoretical statistical model has been constructed to represent the multiphoton dissociation of SF_6 . Based on this model, predicted recoil energy distributions for five,

Fig. 1. (a) Angular distribution of the fragment products, (b) kinematic diagram for fragments of SF_6 . The circles show the total amount of translational energy released (in kcal), when the SF_5 is found in the phase space which lies on the circle. (XBL 769-10330)

The statistical model is also consistent with an estimate of the dissociative lifetime of excited SF_6 in our apparatus. As described above, for normal laser pulse lengths of 60 ns, only fragments associated with the primary product, SF_5 , are observed. However, when the laser pulse length is widened to 300 ns, SF_5^+ is no longer observed; instead, SF_3^+ , SF_2^+ and F^+ are seen with the same, broadened angular distribution. This indicates that SF_5 is formed during the period of the long laser pulse, and that this incipient SF_5 undergoes secondary absorption and decomposition to SF_4 . Thus, the upper limiting lifetime for the multiphoton dissociation of SF_6 at a power density of 500 MW/cm^2 is 300 ns. The RRKM lifetimes associated with five, six and seven photons in excess of the dissociation threshold are given in Table 1. The agreement

Recoil energy kcal mole ⁻¹	Relative probabilities			
	Experimental	Theoretical		
		(5)*	(6)	(7)
1	0.100	0.104	0.100	0.096
2	.057	.052	.053	.055
3	.031	.024	.028	.031
4	.016	.011	.014	.017
5	.006	.004	.006	.009
6	.003	.002	.003	.005
Lifetimes(ns):	60-300	290	72	22

of both the recoil energy distribution and lifetime estimate with RRKM prediction, suggests that the absorption and decomposition processes involved in the multiphoton dissociation of SF₆ proceed statistically.

Y. T. Lee and Y. Ron Shen

A tunable IR laser, and a neodymium YAG laser pumped optical parametric oscillator will be acquired in 1977. With this laser we will be able to investigate the process of the decomposition of van der Waal's molecules as a potential scheme for effective laser isotope separation. The crossed molecular beam-laser machine is in excellent condition. The formation of van der Waal's molecules in the molecular beam has been investigated quite thoroughly. A tunable IR laser has been the only missing component for this project.

Our effort in the study of multiphoton dissociation process will move from SF₆ to other molecules. In addition to the measurements of recoil velocity and angular distributions, we will also investigate possible production of electronically excited fragments. In order to fully understand multiphoton excitation and dissociation process, we are going to initiate two laser multiphoton dissociation experiments with two lasers operated at different frequencies, powers and delay times.

The third scheme of our molecular beam isotope separation process, the selective process which is based on the modification of sticking coefficients of molecules by laser excitation, will also be carried out in 1977.

5. 1976 PUBLICATIONS AND REPORTS

Y. T. Lee and Y. R. Shen

1. See Y. T. Lee in Molecular Sciences Section,
p. 370.
2. See Y. R. Shen in Materials Sciences Section,
p. 142

b. Selective Photochemistry

C. Bradley Moore, Principal Investigator

1. EXOTHERMIC HALOGEN ATOM-HALOGEN HALIDE REACTIONS

Chang-Chi Mei

The reactions $\text{Cl} + \text{HI}$ and $\text{Cl} + \text{HBr}$ are typical of reactions with a heavy-light-heavy mass combination and belong to a family of systems ($\text{F} + \text{HCl}$, etc.) for which laser action has been established. These are also the microscopic reverse of reactions recently used to demonstrate separation of halogen isotopes. Understanding the dynamics of these reactions is therefore of great interest. The reactions have been studied in the past by a variety of techniques. Nevertheless, there are still not enough data to determine many important features of the reaction hypersurfaces. In fact, actual rate constants for these reactions had not even been measured.

To provide more information about the reaction dynamics, we have measured the reaction rates of $\text{Cl} + \text{HI}$ and $\text{Cl} + \text{HBr}$ over the temperature range 218 to 402 K by photolyzing Cl_2 with pulsed N_2 -laser and following the rate of reaction via the time-resolved infrared chemiluminescence of the excited product HCl molecules. Semilogarithmic plots of reaction rate and cross section of $\text{Cl} + \text{HI}$ and $\text{Cl} + \text{HBr}$ as a function of temperature are shown in Figs. 1 and 2, respectively. The

Fig. 1. Semilog plot of rate constant K_1 and cross section $\sigma_1 = K_1/\bar{v}$, for the reaction $\text{Cl} + \text{HI}$ vs. $10^3/T$. Circles: experimental rate constant. Triangles: cross section. The error bar shows one standard deviation. (XBL 7612-4589)

Fig. 2. Semilog plot of rate constant K_2 and cross section σ_2 for the reaction $\text{Cl} + \text{HBr}$ vs. $10^3/T$. Circles: experimental rate constants. Triangles: cross section. The error bar shows one standard deviation. (XBL 7612-4588)

anomalous behavior of the temperature dependence can be explained by a simple bimolecular collision with an energy barrier (the Arrhenius equation) or with a purely attractive potential. However, rotational energy as well as translational energy may play an important role in changing the reaction cross section.

An explanation of the anomalous temperature dependence may be given by the following model for the reaction. This model is based on the high polarizability of the I (or Br) atom and the small moment of inertia of the HI (HBr) molecule. During the reaction, the Cl atom collides with the I atom that has a strong attractive potential, forming an H-I-Cl transient reaction species. The reaction is complete when the H atom migrates across to the Cl atom. The preferred configuration of the transient H-I-Cl species could cause a small energy barrier to H atom rotation between the I and the Cl atoms. At low temperature the barrier hinders the reaction and thus the rate increases with increasing rotational temperature of the molecule; this accounts for the rise in cross section from the right of the curve.

However, increased translational temperature reduces the lifetime and probability of formation of H-I-Cl and hence decreases the reaction cross section. Additional understanding of the mechanism involved in this model can be obtained by a rotational energy dependence study at fixed translational temperature and by detailed molecular beam studies. This understanding is important for the construction of the intermolecular potential energy surfaces and the dynamics of collisions on these surfaces.

2. $\text{ICl}(A^3\Pi_1) + \text{H}_2$ PHOTOCHEMISTRY

S. J. Harris

Laser photochemistry holds promise not only for possible synthetic uses but also for the understanding of the role of internal energy in promoting chemical reactions. Ideally one would like to study a system of reactions which are inert in the absence of light and which react in its presence. One of the reactants should absorb at a laser wavelength and go to a well defined excited state or states. Finally, excitation should not induce dissociation or predissociation, since then internal energy selection is lost. Such a system is $\text{ICl} - \text{H}_2$. Like the $\text{I}_2 - \text{H}_2$ and $\text{Cl}_2 - \text{H}_2$ systems, there is no reaction in the dark at room temperature. ICl absorbs light considerably to the red of its dissociation limit at 574 nm to the $A^3\Pi_1$ state whose spectrum has been completely analyzed.

The reaction goes as follows:

HCl and HI are formed the latter immediately reacting with ICl to form HCl and I_2 . Thus, 2 molecules of HCl are formed in each reaction, and the quantum yield is defined by

$$\Phi = \left(\frac{1}{2}\right) \frac{\text{no. HCl produced}}{\text{no. photons absorbed}}.$$

It is found that Φ (typically 0.2 - 0.4%) is only weakly a function of the initial vibrational level between $\lambda = 577$ and 625 nm. The reaction run at the shortest wavelength, $\sim 1/2$ kT below dissociation, shows that Cl atom reactions (e.g., $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$, etc.) are not important, since Φ does not get very large at this wavelength.

Φ does drop to nearly 0 if the ratio H_2/ICl is as low as ~ 1 . This is because ICl^* is quenched by ICl with every collision, whereas H_2 needs ~ 25 collisions to quench ICl^* . Assuming that only ICl^* is reactive, the rate constant for $\text{H}_2 + \text{ICl}^* \rightarrow \text{HCl} + \text{HI}$ is found to be $\sim 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$.

This new type of photochemical reactions is important because no radicals are involved and the excitation could be isotopically selective. Reactions without free radicals are relatively easy to understand and the kinetics are simple. The isotope scrambling and chain reaction processes involving radicals are avoided. Hence it is an ideal type of reaction for isotope separation.

3. RATE OF ELECTRONIC ENERGY TRANSFER IN FORMALDEHYDE

J. Weisshaar and A. Cabello

Isotopic scrambling of excited species puts an upper limit on the overall efficiency of isotope separation schemes involving selective electronic excitations. A major cause of such scrambling processes may be transfer of electronic energy during collisions. A knowledge of energy transfer rates is required for accurate estimates of the isotope enrichment factor in these schemes.

We have measured the rate of electronic energy transfer from the $^1A_2(S_1)$ excited state of H_2CO to D_2CO under single vibronic level excitation conditions. By carefully choosing the wavelength of a pressure-tuned, N_2 -laser pumped dye laser (bandwidth $\sim 0.5 \text{ \AA}$), we can selectively excite H_2CO in a mixture of H_2CO and D_2CO with an excitation ratio of ~ 25 . The total fluorescence of the mixture is monitored as a function of time. H_2CO fluorescence is discriminated from D_2CO fluorescence on the basis of timescale; at a few Torr, H_2CO typically decays ~ 5 times faster than D_2CO . By comparing the amplitude of the slow (D_2CO) decay in the mixture to that of pure D_2CO excited under the same conditions at its partial pressure in the mixture, we can determine the rate constant for electronic energy transfer.

Figure 1 shows the log plot of the total fluorescence of a mixture of 1.02 Torr H_2CO + 2.06 Torr D_2CO after excitation of the 4_1^0 (vibrationless) level of H_2CO at 3687 $\text{\AA}$. Also shown is the decay of 2.09 Torr D_2CO . From the $t=0$ intercepts, we can determine the rate of electronic energy transfer to be $0.12 \mu\text{s}^{-1} \text{ Torr}^{-1}$, or about 1% of the gas kinetic collision rate. For excitation to the 4_0^3 band of H_2CO (3430 $\text{\AA}$), the analysis is more difficult due to multiple exponential decays. We can only set an upper limit of $\sim 0.2 \mu\text{s}^{-1} \text{ Torr}^{-1}$ for the total energy transfer rate from H_2CO^* to D_2CO ; clearly no dramatic increase in rate has occurred for the higher excitation.

Marling¹ has recently made a thorough study of the potential of the formaldehyde predissociation scheme using fixed frequency ion lasers to separate carbon, hydrogen, and oxygen isotopes in macroscopic quantities. He found that for HDCO excited at 3372.5 $\text{\AA}$ (an excitation wavelength at which molecular products dominate) the total probability for isotopic scrambling was between 0 and 6%. HD enrichment factors of ~ 25 were obtained. There are two possible contributions to such scrambling.

Fig. 1. Log plot of total fluorescence intensity vs. time for a mixture of 1.02 Torr H_2CO + 2.06 Torr D_2CO , as well as 2.09 Torr D_2CO . Excitation is to the 4_1^0 band of H_2CO at 3687 Å. (XBL 7612-4590)

The first is electronic energy transfer, the process of interest here; the second is collisional dissociation of the undesired isotope by an excited state molecule of the desired isotope. In our experiment only the former process is monitored. We find an energy transfer probability between 0 and 2%. The isotopic scrambling may be entirely due to energy transfer; scrambling is in any case very small.

This study is of fundamental interest in terms of understanding the mechanisms of electronic energy transfer in polyatomic molecules. The often-invoked Förster dipole-dipole interaction theory would predict much higher rates for the 4^3 band than for the 4^0 band due to improved Franck-Condon factors. Such a difference is not observed. The insensitivity to Franck-Condon factors indicates that energy transfer process may involve close range collisions. Additional work, both experimental and theoretical, is necessary for further understanding of this process.

1. J. B. Marling, Preprint UCRL-78317 Rev 1., 1976.

4. LABORATORY FACILITIES

A. H. Kung

In its second year of operation our facilities have been sufficiently completed for research to

go forward at close to 100% capacity. The development of a pressure tuned N_2 -laser pumped dye laser is nearly complete. Performance of the laser is within expectation. Operating in an oscillator-amplifier configuration, the laser puts out a peak power of 60 kW in 5 nsec pulses and is tunable from 3600 Å to 7100 Å. Insertion of a 2.5 mm air gap etalon has helped reduce the linewidth of the laser to less than 0.03 Å which is the instrument resolution of our monochromator. By varying the air pressure of the laser cavity from 1 atm to 5 atm we have continuously tuned over 5 Å (40 cm^{-1}) around 3700 Å. The same amount of pressure tuning is expected for the entire visible and UV range. Along with our PDP-Tektronix signal averager, the laser has been in use for the formaldehyde energy transfer and quenching experiments.

Another system, which represents the latest development in solid state laser and tunable laser technologies, has been designed and is under construction. The expected performance characteristics are shown in Table 1. It involves a high average power q-switched Nd:YAG laser-amplifier to be used as the pump laser. The fixed wavelength at 1.06 μm of the Nd:YAG laser is converted to tunable infrared wavelengths from 1.4 μm to 4.3 μm using an angle-tuned LiNbO_3 parametric oscillator. Overall photon conversion efficiency of 10% or better is expected with an output linewidth of $\leq 0.1\text{ cm}^{-1}$. This represents at least 500 kW of tunable narrowband infrared energy and will be useful for studies of multiphoton excitation processes and selective excitation of high vibrational levels. The high average power will yield macroscopic amounts of IR photochemical reaction products.

The Nd:YAG laser can also be converted into a tunable visible system via frequency multiplication and a dye oscillator-amplifier combination. As

Table 1. Characteristics of the Nd:YAG laser system

	Nd:YAG pump Laser	LiNbO_3 parametric oscillator	dye laser	H_2 Raman Laser
wavelength (μm)	1.06	1.4 to 4.3	.36 to .71	.299
pulsewidth (nsec)	20	10	15	10
rep rate (pps)	10	10	10	10
energy/pulse (mJ)	300	15 at $\sim 2\text{ }\mu\text{m}$	15 at .58 μm	10
peak power (MW)	15	1.5	1.0	1.0
linewidth (cm^{-1})	.5 ($< .1$ with etalon)	$\leq .1$	$\leq .05$	.5
pump wave- length (μm)	-	1.06	.532 .355 or .266	.266
total energy conversion from pump	-	10% (signal and idler)	20%	30%

such the system will be used for isotopically selective photolyses, studies of exothermic hydrogen halide-halogen reactions, and a variety of problems in selective reaction dynamics.

We have initiated an investigation of the physical processes involved in selective multiphoton dissociation of molecules. Recently, this dissociation method has been demonstrated to be effective in achieving isotope separation. A tunable TEA-CO₂ laser has been constructed for this investigation. A spectrophone cell similar to one used in Letokhov's group in Moscow has been built and will be used to determine the particular transitions of the CO₂ laser that will induce the maximum multiphoton excitation. Experimental tests of this system on SF₆ are nearly complete.

5. RESEARCH PLANS FOR CALENDAR YEAR 1977

C. Bradley Moore

Multiphoton Excitation and Dissociation. Using a combination of infrared fluorescence, resonance Raman and electronic absorption spectroscopy as diagnostic tools, we plan to study the kinetics through which multiphoton excitation and dissociation occur. Initial experiments involve using a TEA CO₂ laser to establish nonlinear absorption and dissociation of molecules including d₂-formaldehyde, d₁-formaldehyde, glyoxal, propynal and ClO₂. Following excitation, the internal energy distribution, rate of internal energy transfer, role of collisions on dissociation and chemical reactivity of excited molecules will be studied. The new YAG pumped OPO system is an essential capability in these studies.

These studies should give a very good understanding of the excitation and dissociation processes and would complement the molecular beam work and the feasibility studies of the LIS program.

Chemical Reactions of Selectively Excited Molecules. The chemistry of electronically excited halogen molecules will be studied. We believe we have discovered a new type of electronically excited bimolecular photochemical reaction: $\text{ICl}^* + \text{H}_2 \rightarrow \text{HCl} + \text{HI}$. The quantum yield and kinetics of this reaction will be studied as a function of various parameters like excitation wavelength and reagent pressure. Other halogens will also be pursued. With the powerful YAG-pumped OPO and dye laser many new chemical systems can be studied and will yield enough products for chemical analysis. We will study reactions of highly vibrationally excited states of hydrogen halides and of azo and diazo compounds. These reactions may prove useful for isotope separation.

6. 1976 PUBLICATIONS AND REPORTS

C. Bradley Moore and Associates

Journals and Conference Proceedings

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- *2. V. S. Letokhov and C. Bradley Moore, Reviews of Laser Isotope Separation Methods, *Kvantovaya Elektronika*, Vol. 3, No. 2, 248 and Vol. 3, No. 3, 481 (in Russian); *Soviet J. of Quant. Elec.* Vol. 6, No. 2, 129 and Vol. 6, No. 3, 259 (in English) (1976).
- *†3. P. L. Houston and C. Bradley Moore, Formaldehyde Photochemistry: Appearance Rate, Vibrational Relaxation, and Energy Distribution of the CO Product, *J. Chem. Phys.* **65**, 757 (1976).
- *4. S. R. Leone, F. Zaraga, and C. Bradley Moore, Br + Br₂ Atom Exchange: An Isotopically Selective, Laser-Initiated, Chemical Study, *Chem. Phys. Lett.* **42**, 275 (1976).
- *††5. P. Hess and C. Bradley Moore, Vibrational Energy Transfer in Methane and Methane-Rare-Gas Mixtures. *J. Chem. Phys.* **65**, 2339 (1976).
- *†6. A. P. Baronavski, A. Cabello, J. H. Clark, Y. Haas, P. L. Houston, A. H. Kung, J. Reilly, J. C. Weisshaar, M. B. Zughul and C. Bradley Moore, The Photophysics and Photochemistry of Formaldehyde. Proceedings of the Tunable Lasers and Applications Conference, Loen, Norway (1976). Eds. Springer Verlag.
- *7. E. S. Yeung and C. Bradley Moore, Isotopic Separation by Photopredissociation. U.S. Patent # 3,983,020, Sept. 28, 1976.
- †8. C. Dasch, Branching Ratios in Vibrationally Inelastic Collisions. *Bull. Am. Phys. Soc.* **21**, (11) 1289 (1976).
- *†9. J. M. Wiesenfeld and C. Bradley Moore, Vibrational Relaxation of HCl (v = 1,2) Isolated in Solid Ar. *Bull. Am. Phys. Soc.* **21**, (11) 1289 (1976).
- †10. R. G. Macdonald and C. Bradley Moore, Vibrational Relaxation of DCl (v = 1) by Cl and Br Atoms and of HBr (v = 1) by Br Atoms. *J. Chem. Phys.* (1976).

Invited Lectures

1. Materials and Molecular Research Division Review Presentation.

2. ERDA Advanced Concepts in Isotope Separation Workshop.
3. Japan-U.S.A. Seminar on Molecular Energy Transfer, Tokyo, Japan.
4. California Institute of Technology (Chemistry Colloquium).
5. University of California, San Diego (Physical Chemistry Seminar).
6. Tunable Lasers and Applications Conference, Loen, Norway.
7. Am. Chem. Soc., National Meeting, San Francisco (Symposium on Laser Isotope Separation).

8. Am. Phys. Soc., National Meeting, Stanford, (Symposium on Applied Physics).
9. Laser Chemistry Conference, Steamboat Springs, Colorado by R. G. Macdonald.

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[†]Partially sponsored by the U.S. Army Research Office-Triangle Park

[‡]Partially sponsored by the U.S. Air Force Office of Scientific Research.

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V.

Conservation

CONSERVATION

a. Development of Electrochemical Synthesis and Energy Conversion

R. H. Muller, J. Newman, C. W. Tobias, Principal Investigators

Major advances in electrochemical reaction technology are required to achieve recognized national goals in developing economical methods for the storage of electrical energy and improving the efficiency of electrochemical energy use for the recovery of basic metals and the production of chemicals.

Transport phenomena in electrolytes and at electrode surfaces are being analyzed, since the transport of charge and mass, and the distribution of reaction rates on electrode surfaces and in the depth of porous electrodes are decisive factors in determining the performance of electrochemical processes. The transformation of surface layers is being investigated because of its importance in the operation of primary and secondary batteries. The advancement of new concepts of cell design and operation is undertaken to further progress in the design of galvanic cells and in industrial electrolysis.

The overall aim of this program is to improve the energy efficiency, lower the capital cost and increase the materials yield of electrochemical cell processes employed for the reversible conversion of chemical to electrical energy in galvanic cells and for the production of materials by electrolysis.

1. PROCESS DEVELOPMENT FOR THE ELECTROWINNING OR REFINING OF POTASSIUM METAL

Henry Law and Charles W. Tobias

This project is aimed at establishing the feasibility of an entirely new technology for the production of alkali and alkaline earth metals by electrolysis at ambient temperatures. It includes (a) development of solvent purification and solute dehydration adaptable for large-scale use; (b) establishment of solvent stability; (c) design of technically feasible transfer of amalgam from aqueous to nonaqueous electrolyte; (d) search for suitable anodic reactions for the primary recovery of alkali metals.

Electrodeposition of potassium from propylene carbonate-KAlCl₄ electrolyte was proposed as a method for electrowinning or refining the metal.^{1,2} To evaluate economic viability, investigations during the past year were focused on overpotential behavior, solvent stability and on materials suitable for cell components.

Measurements of overpotential were carried out in the 24° to 68°C range by a current interruption

technique. Strong decline of overpotential was observed (Fig. 1) above the melting point of potassium (M.P.: 63.65°C). Continuous potassium

Fig. 1. Potassium reduction from 0.5 M KAlCl₄-propylene carbonate solution. Overpotential as a function of current density and temperature. (XBL 771-7315)

deposition-dissolution experiments were performed over periods of up to 24 days without any evidence of solvent attack. It is therefore concluded that the process could be run above the melting point of potassium, a feature which could make the removal of the metal from the cell rather convenient. As materials of construction a number of polymeric materials are stable in contact with the electrolyte and the metal. Polypropylene shows the greatest promise. Nafion membranes were used to separate the two halves of the H-type experimental cells; these demonstrated good stability and comparatively low resistance. Stainless steel is suitable for cathode construction. On the basis of these findings, a 1-ampere cell is being designed as a stage in scale-up. The purification procedure involving treatment with either activated carbon or alumina, followed by vacuum distillation of the commercial solvent,

is sufficiently simple; further work in this area is not necessary at this stage of development of the overall process.

1. Charles W. Tobias and Jacob Jorne, Method of Production of Alkali Metals and their Alloys, U.S. Patent No. 3,791,945. Assigned to the USAEC, 1973.

2. Radoslaw Atanasiowski, Henry Law, and Charles W. Tobias, An Ambient Temperature Process for Reduction of Potassium Metal, MMRD Annual Report for 1975, LBL-4550, p. 165.

2. ANODIC SURFACE LAYERS

The purpose of this project is to provide direct experimental evidence about properties and modes of formation of anodic surface layers on materials of interest for battery application by the use of newly-developed techniques for *in situ* observation of electrode surfaces. Observational tools include a unique fast, self-compensating ellipsometer,¹ ultrahigh vacuum equipment for the combination of ellipsometry with ion-etching and Auger spectroscopy and a laser interferometer with greatly refined data evaluation procedures. Properties of surface layers, such as thickness, composition and porosity, and their dependence on reaction conditions, will be determined in order to find means for the consistent generation of layers with desirable electrochemical properties.

a. Formation of Anodic Surface Layers on Battery Materials

Craig G. Smith and Rolf H. Muller

Preliminary observations on the anodic dissolution of Zn, Ag, and Cu in alkaline solutions have determined the feasibility of an extended study. Figure 1 illustrates how different

Fig. 1. Sequence of processes in the anodic dissolution of Zn at constant potential observed by ellipsometry. Horizontal anode facing down, polycrystalline Zn, 1.0 V vs. Hg/HgO, 0.5 M KOH. (XBL 768-3283)

optically dominant processes can be identified in succession during the oxidation of Zn in aqueous KOH. The processes are initial roughening of the surface, accumulation of soluble species in the solution adjacent to the electrode, and formation of an optically absorbing film that leads to passivation.²

Techniques have now been refined by the use of single crystal electrodes of Zn, Ag, Cd, Pb and Cu, in order to reduce roughening of the metal surface during reaction. Natural convection effects have been minimized by re-arranging the ellipsometer for use with horizontal electrodes facing up. Electrode-electrolyte combinations have been used to provide the widest-possible range of solubilities of the primary reaction products (0.5 - 6 M KOH, 1 M H₂SO₄), which allowed the application of controlled current densities between 5 μ A/cm² and 0.5 A/cm².

The range of experimental conditions was chosen to allow the development of a comprehensive viewpoint of anodic film formation. The detailed interpretation of the experimental observations presently in progress, will seek to establish dynamic events of film formation for different materials and operating conditions and their effect on the properties of the resulting products.

1. R. H. Muller, Surface Sci. **56**, 19 (1976).
2. R. W. Powers, J. Electrochem. Soc. **118**, 685 (1971).

b. Passivation of Lithium in Battery Electrolytes

Richard D. Peters and Rolf H. Muller

Lithium is employed in several aqueous and nonaqueous batteries of high energy density.^{1,2} The formation of passivating surface layers is essential for the functioning of many of these batteries but can also severely restrict their performance. This is particularly the case for the lithium-water system for which porous layers of LiOH and Li₂O have been postulated.³

The feasibility of using ellipsometry for the *in situ* observation of Li anodes is being investigated. Of particular interest are formation and properties of desirable surface layers on Li in H₂O which greatly reduce the rate of spontaneous, non-electrochemical reactions and properties of undesirable layers that inhibit the delivery of electrical power.

Optically smooth, flat surfaces have been prepared by controlled dissolution of the metal mounted in electrode holders, using methyl ethyl ketone in an argon atmosphere. Facilities for the circulation of aqueous LiOH solutions have been built.

1. M. Eisenberg and K. Wong, Stable High Energy Non-Aqueous Electrolyte-Lithium Batteries, Proc.

8th Intersociety Energy Conversion Engr. Conf., Philadelphia, Pa (1973).

2. E. L. Littauer and K. C. Tsai, Electrochemical Characteristics of the Lithium/Aqueous Electrolyte/Passive Cathode Battery System, 26th Annual Proc. Powder Sources Conf., p. 57, (1974).

3. E. L. Littauer and K. C. Tsai, Anodic Behavior of Lithium in Aqueous Electrolytes, J. Electrochem. Soc. 123, 771 (1976).

c. Construction of Ultrahigh Vacuum System

Craig G. Smith, Walter T. Giba and Rolf H. Muller

Although ellipsometry is very sensitive to small amounts of foreign materials on surfaces, variations in film properties normal to the surface can usually not be determined unambiguously. Also, the chemical composition of surface

layers can often not simply be derived from the optically-determined refractive index, particularly if porosity is a factor, too.

In order to augment ellipsometer data, an ultrahigh vacuum system has been built in which surface layers can gradually be thinned by ion etching, while being observed by ellipsometry. Elemental composition at different stages of thinning can be determined by Auger spectroscopy without realignment of the specimen. The optical windows of the chamber can be aligned to be normal to the light beam. The whole vacuum system can be readily removed from and reconnected to the ellipsometer (Fig. 2). With this equipment, we expect to be able to determine composition--and porosity profiles of surface layers which can be transferred without alteration into a vacuum environment.

Fig. 2. Equipment for the combined use of ellipsometry, ion etching, Auger spectroscopy and LEED in surface studies. (CBB 7612-11054)

3. SURFACE MORPHOLOGY OF METALS IN ELECTRO-DEPOSITION

Milan Jaksic, Andrew Kindler, Geoffrey Prentice and Charles W. Tobias

This program is aimed at the elucidation of the role of the electric field and of solution-side mass transport in the macrocrystallization of metals. Of particular interest are the mechanisms by which surface imperfections grow and propagate, leading to rough, powdery or treeing deposits.

(a) A mathematical model describing the surface profile of a cathode undergoing electrodeposition

was formulated. The model describes changes of the surface geometry as a function of time for an initially sinusoidal profile subjected to a primary current distribution. Models were also established for a cathode that includes an external 90° corner, and for one containing a cylindrical hole. Although the modeling procedures have been successfully tested, further refinements in the computer-implemented numerical solution of the Laplace equation are needed to improve precision and to increase the rate of convergence.

(b) A study of the morphology of electrodeposited zinc was initiated to evaluate the role

of electrolyte properties and of mass transport. Zinc is deposited onto highly polished platinum, nickel or pyrolytic graphite rotating disk electrodes. Concentration of electrolyte, current density, and rotational speed are varied over broad ranges. Using potential sweep voltametry, clearly defined limiting currents were only found in the presence of excess supporting electrolytes. In acid solutions, hydrogen evolution catalyzed by zinc black, obscured limiting currents. Deposits tend to be smooth at higher current density and low acidity ($\text{pH} = 4.5-5$), while they show ridges in characteristic radial swirl patterns, already well below the limiting current density, at higher levels of acidity ($\text{pH} < 4$) (Fig. 1).

(a)

(b)

Fig. 1. Effect of pH on the surface texture of zinc electrodeposited from 0.1 M ZnCl_2 on a rotating platinum disk. pH adjusted by addition of HCl. Diameter: 11.28 mm; Current density: 10 mA/cm^2 ; Time: 2 hours. (a) 100 rpm, $\text{pH} = 5.1$; (b) 180 rpm, $\text{pH} = 3.8$. (XBB 771-350)

4. ANALYSIS AND SIMULATION OF ELECTROCHEMICAL SYSTEMS

Modeling is being applied to electrochemical systems for the purpose of determining the important factors which govern the behavior of the system and of optimizing the use of energy and capital. Fundamental information about thermodynamics, transport processes and electrochemical reaction kinetics serves as input for the models. Current distributions, energy and material efficiencies are derived for different reactor configurations and operating conditions.

a. Simulation of a Packed Bed as an Array of Periodically Constricted Tubes I: Creeping Flow

Peter Fedkiw and John Newman

A general method¹ has been developed to solve the creeping-flow equations in a continuous, periodic, arbitrarily shaped tube. Interior collocation on a finite-difference grid was used to solve the Stokes stream function equation. Results are presented for a parabolic and a sinusoidal periodically constricted tube (PCT). A friction factor, Reynolds number relationship for a packed bed modeled as an array of sinusoidal PCT has been calculated.

1. Peter Fedkiw and John Newman, Simulation of a Packed Bed as an Array of Periodically Constricted Tubes I: Creeping Flow, LBL-5199, July 1976.

b. Simulation of Packed Bed as an Array of Periodically Constricted Tubes II: Developed Mass Transfer at High Péclet Number in Creeping Flow

Peter Fedkiw and John Newman

The convective diffusion equation for a limiting reactant with a large Péclet number has been solved for the asymptotic Sherwood number in a periodically constricted tube (PCT).¹ The analysis yields a Graetz-like eigenvalue problem which is valid for any arbitrarily shaped PCT. The results depend upon two ratios of period length, average radius, and sinusoidal amplitude.

1. Peter Fedkiw and John Newman, Simulation of a Packed Bed as an Array of Periodically Constricted Tubes II: Developed Mass Transfer at High Péclet Number in Creeping Flow, LBL-5406, July 1976.

c. Simulation of a Packed Bed as an Array of Periodically Constricted Tubes III: Low Péclet Number, Asymptotic Sherwood Number

Peter Fedkiw and John Newman

It can be shown that the concentration field in a packed bed reactor satisfies Laplace's equation to first order at a low Péclet number. This then results in the Sherwood number becoming linearly dependent upon the Péclet number as

$Pe \rightarrow 0$. Assuming the sinusoidal PCT model for a packed bed, the bed Stanton number has been calculated.

d. Removal of Heavy Metal Ions from Dilute Streams Using Flow-Through Porous Electrode Reactors

James A. Trainham and John Newman

Three metal ions in particular are being considered: Hg^{++} , Pb^{++} , and SbO^+ . As reported last year, the results on the removal of Hg^{++} ions from brine solutions has been quite successful using a porous carbon bed.

Since measurement of the effective specific interfacial area is difficult for carbon beds, more fundamental studies using stainless steel spheres are being conducted.

Problems of channeling due to hydrogen evolution have been anticipated in the removal of Pb^{++} ions and a high-pressure reactor has been built which will keep hydrogen dissolved in the solution.

e. A Thermodynamic Estimation of the Minimum Concentration Attainable in a Flow-Through Porous Electrode

James A. Trainham and John Newman

The minimum concentration attainable in a porous flow-through reactor is estimated by applying thermodynamics of electrochemical cells with a knowledge of the maximum reactor operating potential.¹ This predicted concentration is the equilibrium wall concentration at the back of the reactor and is qualitatively compared to the experimentally measured minimum average bulk values observed by various authors for the deposition of copper, silver, lead, and mercury, and for the oxidation of ferrous ions. It is suggested that a knowledge of the current vs. reactor operating potential will elucidate lower limits observed for any metal system. In particular, the case of antimony removal is discussed.

1. James Trainham and John Newman, The Minimum Concentration Attainable in a Porous Flow-Through Electrode Reactor, LBL-5171, June 1976.

f. A Flow-Through Porous Electrode Model: Application to the Removal of Metal Ions from Dilute Streams

James A. Trainham and John Newman

A one-dimensional model for flow-through porous electrode reactors operating below the limiting current has been developed. The model assumes that there is one primary reactant species in an excess of supporting electrolyte and that simultaneous side reaction may occur. The con-

ductivity of the matrix and pore phases is assumed to be constant. These assumptions not only simplify the analysis, but make the model attractive for design purposes. The model predicts nonuniform reaction rates due to ohmic, mass transfer, and heterogeneous kinetic limitations; the effect of axial dispersion is included. Satisfactory results are obtained between model predictions and experimental data on the removal of copper.

5. RESEARCH PLANS FOR CALENDAR YEAR 1977

R. H. Muller, J. Newman, and C. W. Tobias

(a) Process Development for the Recovery of Metallic Potassium. A 1-ampere cell for the deposition of potassium from $KAlCl_4$ in propylene carbonate will be designed and put into operation. The anodic reaction will either be the dissolution of potassium from its amalgam, or the sacrificial dissolution of aluminum to form $AlCl_3$ according to the net reaction: $3KCl + Al = 3K + AlCl_3$. Provisions will be made for the collection and removal of molten metal from the cell to facilitate precise measurements of current efficiency.

(b) Anodic Surface Layers. The modes of formation, structure and composition of anodic surface layers on metals will be elucidated by in situ ellipsometer measurements. The effect of electrode potential, solubility of primary reaction products, crystal orientation and mass transport conditions on properties of the layers (porosity, chemical composition, multiple layers) will be investigated in combination with scanning electron microscopy, ion etching and Auger spectroscopy. The observation of Li in flowing aqueous LiOH by ellipsometry will be initiated.

(c) Surface Morphology of Metals in Electrodeposition. Mathematical modeling of small-scale surface profiles will be extended to include a variety of shapes of imperfections usually encountered in metal deposition practice. Surface roughness formed in copper deposits will be determined as a function of composition, flow rate, and current density in a large channel electrolyzer equipped to handle flow to $Re = 150,000$. The initiation and propagation of surface roughness in zinc deposition from acid solutions will be studied using a rotating disk electrode and a planar electrode imbedded into the wall of a flow channel.

(d) Analysis and Simulation of Electrochemical Systems. A high Peclet number, low Reynolds number mass transfer correlation in a packed bed will be experimentally determined for comparison with theoretical predictions. This correlation will be useful in determining an upper limit for the removal rate of dilute contaminate from waste streams in porous flow-through electrodes. The correlating parameters will be velocity, porosity, bed length, Schmidt number and specific interfacial area.

6. 1976 PUBLICATIONS

R. H. Muller, J. Newman, and C. W. Tobias

Refer to publications in other sections as follows:

Mass and Charge Transport: Charles W. Tobias,
Principal Investigator, p. 182.

Electrochemical Phase Boundaries: Rolf H.
Muller, Principal Investigator, p. 211.

Electrochemical Systems: John Newman,
Principal Investigator, p. 257.

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VI.

Appendix

MATERIALS AND MOLECULAR RESEARCH DIVISION STAFF — 1976

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 E. Skrydlinski - Staff Assistant - Personnel
 S. Stewart - Staff Assistant - Purchasing

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ΔJ. Boehlert	S. Jennings	M. Penton
G. Brazil	R. Jones	ΔE. Radmilovic
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P. Bucksbaum	ΔR. Holthuis	D. MacDonald	ΔR. Sharp
ΔK. Carey	T. Howard	ΔT. Marsh	ΔM. Singer
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E. Dittmar	D. Jurica	ΔA. O'Keefe	ΔL. Wachs
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