INORGANIC MATERIALS RESEARCH DIVISION Annual Report 1972

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Chemistry

Solid-State
Physics

Chemical
Engineering

Ceramic
Engineering

Metallurgical
Engineering

Metallurgical
Engineering

INORGANIC MATERIALS RESEARCH DIVISION
ANNUAL REPORT, 1972

April 1973

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GENERAL INTRODUCTION

Leo Brewer, Division Head
Victor F. Zackay, Associate Head
Rolf H. Muller, Assistant to Division Head

During 1972, 21 Ph.D., one Doctor of Engineering and 16 M.S. degrees were awarded to INRD students and 189 journal articles or book chapters were published including 18 articles based on work supported by agencies other than the Atomic Energy Commission--D.O.T., N.S.F., O.N.R., U. S. Army, and A.F.O.S.R. The level of support by other agencies now amounts to approximately 11% of the total INRD budget. The number of postdoctorals is at an all-time high of 45 due to the Presidential Internships and Public Employment Program (PEP) fellows and an increased number of sabbatical visitors offsetting the reduction in funds available for postdoctoral positions. The number of graduate students has remained roughly level at about 180 for the past five years. The availability of positions for our graduates at both the M.S. and Ph.D. levels has dramatically improved this last year and we again have the situation of students with many job offers.

Ralph Hultgren retired officially on July 1, 1972, but the completion of Vol. I. Selected Values of the Thermodynamic Properties of the Elements and Vol. II. Selected Values of the Thermodynamic Properties of Binary Alloys, took all of his time through the end of the year. He will continue to work part time on the maintenance of an up-to-date bibliography for the thermodynamic properties of metals and alloys.

Professor Alexander Pines has become associated with the division during this year. He came from Massachusetts Institute of Technology where he received his Ph.D. degree in 1972 under the direction of Professor J. S. Waugh. His previous education had been at the Hebrew University, Jerusalem. He has been very productive with 22 publications to date and has started the development of a nuclear magnetic-double-resonance program designed to increase sensitivity sufficiently to study structural and dynamical features of impurities in solids and many other NMR measurements not yet accessible.

As in the past, a number of Inorganic Materials Research Division principal investigators are participating in the University

administration. Professor Victor Zackay is Associate Dean and Professor Joseph Pask is an Assistant Dean of the College of Engineering. Professor Rollie Myers is Assistant Dean of the College of Chemistry, and Professor Charles Tobias was Acting Director of the Art Museum for the Fall quarter and completed his term as Chairman of the Department of Chemical Engineering on July 1, 1972.

Several of the division's investigators received awards and honors in 1972:

Professor Neil Bartlett--honorary Doctorate of Science degree from Colby College, Maine.

Professor Earl Parker--Gold Medal from the American Society for Metals, and the Distinguished Teaching Award by the Department of Materials Science and Engineering.

Professor Charles Tobias--the Edward Goodrich Acheson Award from the Electrochemical Society.

Several investigators are on sabbatical leave:

Professor Marvin Cohen--University of Paris, France (September through June).

Professor Donald Olander--The Institute of Atomic and Molecular Physics, Amsterdam, Netherlands (September through June)

Professor Earl Parker--In residence (September through June)

Professor Yuen-Ron Shen--Harvard University (September through January) (University of Paris, France, remainder of leave)

During the past several years, several principal investigators in the Metallurgy group, have successfully applied fundamental principles of alloy theory, dislocation theory, theories of nucleation and growth, and knowledge of the effects of processing to produce a variety of new and potentially useful materials. Some specific results are the new TRIP steels, new superconducting wire made from powdered niobium and liquid tin containing filaments of Nb₃Sn, low alloy ultra high strength steels with exceptionally high fracture toughness, a strong high temperature material, and a cryogenic alloy more resistant to brittle fracture than any commercially available product.

The success of these investigators encouraged them to establish within the framework of IMRD and LBL, a Center for the Design of Alloys to provide a focus on the efforts within IMRD to create new and useful alloys through the application of basic principles of materials science. The principal investigators who participated in the establishment of the Center were Victor F. Zackay, Earl R. Parker and Milton R. Pickus. Their research efforts are devoted almost entirely to the design of new alloys with superior properties. Shortly before this Annual Review went to press, two more IMRD principal investigators with an interest in alloy design joined the center--they are Gareth Thomas and J. W. Morris, Jr.

The Sixth Annual IMRD Review meeting was held on February 2 and 3, 1972. Reviewers were: Professor C. S. Barrett, University of Denver; Professor Emeritus, J. Chipman, Massachusetts Institute of Technology; Professor W. Klemperer, Harvard University; Professor N. Nachtrieb, The University of Chicago; Professor R. W. Parry, University of Utah; and Professor S. V. Radcliffe, Case Western Reserve University.

SOME HIGHLIGHTS OF THE 1972 RESEARCH PROGRAM

The novel oxidation state of gold $Au(V)$ has been established in the AuF_6^- ion. Salts prepared so far include $Cs^+AuF_6^-$, $O_2^+AuF_6^-$ and $Xe_2F_{11}^+AuF_6^-$. The single crystal X-ray structure of the latter has been determined. It appears that AuF_5 is displaced by SbF_5 from its salts.

(N. Bartlett, p. 12)

Catalysis of hydrocarbon reactions has been shown to take place at an optimum rate on platinum surfaces that are characterized by the presence of ordered atomic steps and an ordered carbon surface structure.

(G. A. Somorjai, p. 25)

Memory filaments in As-Te-I amorphous semiconductors have been identified as whisker-like crystals of tellurium.

A magnetron type sputtering apparatus has been constructed for the production of ZnO films for possible application as a low cost solar photovoltaic cell.

(J. Washburn, p. 97)

General equations for the velocity of a dislocation gliding through a random array of point obstacles at finite temperature have been derived and the thermal "jerkiness" of the motion explained.

A new interpretation of the surface stress

of a simple fluid has been obtained through use of a multipolar model, allowing earlier mechanical models to be reconciled.

(J. W. Morris, Jr., p. 103)

Alloy design to apply spinodal transformation in conjunction with the martensitic transformation has produced high strength dispersions similar to ausforming without use of plastic deformation.

(G. Thomas, p. 108)

Following a study of the microstructural and compositional features that control the toughness and strength at cryogenic temperatures, interstitial-free iron based alloys were designed, containing 12% nickel and varying amounts of titanium. Charpy impact energy values of 150 ft lbs and yield strength of 150 ksi were attained at $-196^\circ C$ in the alloy Fe-12Ni-0.5Ti by heat treatment in a two phase $\alpha+\gamma$ region. In further studies (by Professor J. W. Morris), the titanium content was decreased to 0.25% and the alloy had a Charpy impact value of 172 ft lbs and yield strength of 185 ksi at $6^\circ K$.

(V. F. Zackay and E. R. Parker, p. 122)

Work on optimization of the process parameters of the (IMRD developed) powder rolled superconducting tape has resulted in a six-fold increase in current carrying capacity. It has been established that niobium hydride powder can be used successfully and advantageously in place of elemental niobium. It has also been established that pre-alloyed niobium-zirconium powder can be prepared by hydriding arc melted buttons. This material is desirable for future work on superconducting materials.

(M. R. Pickus, p. 147)

Experimental and theoretical techniques previously used only to study congruent vaporization reactions have been used to study an incongruent decomposition reaction. The present studies on barium sulfate give results qualitatively similar to the previous study with calcite in that reaction rates are of the order of 1% of the thermodynamically allowed rates and unaffected by a layer of oxide product up to 1 mm thick. The rate, however, appears to be limited by a different process than was calcite decomposition.

(A. W. Searcy, p. 155)

A most significant achievement has been the clarification of the $SiO_2-Al_2O_3$ phase diagram. It has been shown that there are several metastable diagrams which have not been previously proposed and that the original Bowen and Greig diagram is the stable one.

(J. A. Pask, p. 160)

The intrinsic nonstoichiometry has been established for the binary system PbZrO_3 - PbTiO_3 . The techniques developed to determine nonstoichiometry make it possible to fabricate lead zirconate titanate ceramics with controlled defect structures.

(R. M. Fulrath, p. 169)

A simple two-cavity dye laser difference frequency generation system has been used to generate tunable far infrared radiation over the frequency range from 5 to 190 cm^{-1} . Since the dye system can be operated in a repetitively pulsed mode, this system provides a practical tunable spectroscopic source. A total of five different types of far infrared resonant modes have been observed in alloys of the antiferromagnetic iron group fluorides $(\text{Fe,Mn})\text{F}_2$ and $(\text{Co,Mn})\text{F}_2$. All of the resonant frequencies are shown to be in good agreement with theory. This work answers a 10-year old question of the source of extra modes sometimes seen in these classical materials.

(P. L. Richards, p. 188)

Pair-quasiparticle potential differences have been observed in superconductors. The results are in good agreement with a theory involving the imbalance of electron-like and hole-like excitations, a situation that has not been previously discussed. The results are applicable to any superconductor which has been disturbed from equilibrium by a current involving a quasiparticle contribution.

(J. Clarke, p. 197)

A tunable dye laser has been used to study resonance Raman scattering and luminescence in solids. Detailed information is obtained simultaneously about the electronic band structure, the phonon spectrum, and the electron-phonon interaction for a number of crystals. The tuning range of the far-infrared output in optical mixing has been extended to a range from 0 to 200 cm^{-1} . Information about the band structures of several semiconductors and metals has been obtained by analyzing the derivative spectra of the solids.

(Y. R. Shen, p. 205)

A. INORGANIC CHEMISTRY

William L. Jolly, Principal Investigator

1. X-RAY PHOTOELECTRON SPECTROSCOPY

a. Chemical Shifts in Boron 1s Binding Energies of Some Gaseous Compounds*

Patricia A. Finn and William L. Jolly

Recently we reported the nitrogen 1s electron binding energies for a series of gaseous nitrogen compounds and correlated the experimental values with calculated atomic charges and thermodynamic data. In this study we have measured the boron 1s electron binding energies of a series of gaseous boron compounds in order to provide data for further tests of the correlation of binding energies with atomic charges and thermodynamic data. We have also compared the boron 1s binding energies with boron-11 nuclear magnetic resonance chemical shifts.

Chemical shifts in boron 1s electron binding energies for gaseous BF_3 , BCl_3 , $\text{B}(\text{OCH}_3)_3$, B_2H_6 , $\text{B}(\text{CH}_3)_3$, BH_3CO , and $\text{H}_3\text{BN}(\text{CH}_3)_3$ are shown to be linearly related to boron atom charges estimated by Pauling, CNDO, and extended Hückel methods. The best correlation is found with the extended Hückel charges, with inclusion of the interatomic "Madelung potential" (average deviation from straight-line relation, ± 0.83 eV). By application of the thermodynamic method (based on the

approximation that $\Delta E = 0$ for the interchange of a pair of equally charged atomic cores between two different chemical species), the chemical shifts are estimated with an average error of ± 0.57 eV. (See Fig. 1.) There is no obvious correlation between the 1s binding energy chemical shifts and published ^{11}B NMR chemical shifts.

* Abstracted from J. Am. Chem. Soc. 94, 1540 (1972).

1. P. A. Finn, R. K. Pearson, J. M. Hollander, and W. L. Jolly, Inorg. Chem. 10, 378 (1971).

b. The Nitrogen 1s Binding Energies of Transition Metal Nitrosyls*

Patricia A. Finn and William L. Jolly

The bonding and electronic structure of transition metal nitrosyls have been frequently studied in recent years. Two limiting situations have been identified: linearly coordinated NO^+ groups and angularly coordinated ("bent") NO groups. We have investigated the X-ray photoelectron spectra of a series of these compounds to attempt correlations of the nitrogen 1s electron binding energy with structure, electronic features, and N-O stretching frequency.

The data are presented in Table I. It was found advantageous to categorize the compounds in terms of the metal d-electron configurations by making the arbitrary assumption that the nitrosyl groups were NO^+ ions. (Although this assumption is illogical for the few compounds that contain "bent" NO groups, we made the assumption to simplify the classification of the compounds.)

We draw the overall conclusion that there is a definite correlation between the nitrogen 1s binding energy of a nitrosyl group and the electron density on that group. Bent nitrosyls have low binding energies. Linear nitrosyls can have either low or high binding energies, depending on the extent of π back-bonding from the metal atom. The binding energies are at least roughly correlated with the N-O stretching frequencies: when one is high or low, so is the other.

Fig. 1. Plot of boron 1s binding energies vs. thermodynamically estimated binding energies. (XBL 716-6854)

Table I. Nitrogen 1s binding energies for some transition metal complexes.

Compound	No. of d electrons	Nitrogen 1s binding energy, (eV)
MoCl ₂ (NO) ₂ (diars)	6	399.6
trans-[CrCl(NO)(diars) ₂]ClO ₄	5	400.7
K ₃ [Cr(NO)(CN) ₅]	5	400.7
[(C ₆ H ₅) ₄ P] ₃ [Mn(NO)(CN) ₅]·3H ₂ O	6	399.7
trans-[RuCl(NO)(diars) ₂]Cl ₂	6	400.0
trans-[FeCl(NO)(diars) ₂](ClO ₄) ₂	6	402.9
Na ₂ [Fe(NO)(CN) ₅]·2H ₂ O	6	403.3
[π-C ₅ H ₅ Cr(NO) ₂] ₂	7	400.7
RhI ₂ (NO)[P(CH ₃)(C ₆ H ₅) ₂] ₂	8	400.3
RhCl ₂ (NO)[P(C ₆ H ₅) ₃] ₂	8	401.5
CoCl ₂ (NO)(diphos)	8	400.7
trans-[FeCl(NO)(diars) ₂]ClO ₄	7	400.0
[Co(NO)(NH ₃) ₅]Cl ₂	8	400.7
trans-[CoCl(NO)(diars) ₂]Cl	8	400.5
[Co(NO)(diars) ₂](ClO ₄) ₂	8	402.3
CoCl ₂ (NO)[P(CH ₃)(C ₆ H ₅) ₂] ₂	8	401.7, 399.6
CoCl ₂ (NO)[P(n-C ₄ H ₉) ₃] ₂	8	401.5, 399.7
[Fe(NO)(diars) ₂](ClO ₄) ₂	7	401.2, 399.6
[RuCl(NO) ₂][P(C ₆ H ₅) ₃] ₂ PF ₆	8	402.6, 400.2
[Rh(NO) ₂][P(C ₆ H ₅) ₃] ₂ PF ₆	10	401.1
[Ir(NO) ₂][P(C ₆ H ₅) ₃] ₂ PF ₆	10	400.2
Co(NO)[P(C ₆ H ₅) ₃] ₃	10	400.0
Co(NO)(CO)[P(C ₆ H ₅) ₃] ₂	10	400.8
Rh(NO)[P(C ₆ H ₅) ₃] ₃	10	400.8
Ir(NO)[P(C ₆ H ₅) ₃] ₂	10	400.3
Ir(NO)(CO)[P(C ₆ H ₅) ₃] ₂	10	399.6
Ru ₃ (NO) ₂ (CO) ₁₀	10	400.4
NiCl(NO)[P(C ₆ H ₅) ₃] ₂	10	399.8
Ni(N ₃)(NO)[P(C ₆ H ₅) ₃] ₂	10	399.6

* Abstracted from Inorg. Chem. **11**, 893 (1972).

c. Nitrogen 1s Binding Energies of Some Azide, Dinitrogen, and Nitride Complexes of Transition Metals*

Patricia A. Finn and William L. Jolly

We have used X-ray photoelectron spectroscopy to determine the nitrogen 1s binding energies of azide, dinitrogen, and nitride complexes of several transition materials. Such data are of interest because the binding energy shifts can be interpreted in terms of the interaction of the ligands with the transition metal atoms. The data are presented in Table I.

The results indicate that the internal bonding of the azide ion is essentially unaffected by coordination to a transition metal atom; that is, the azide ion appears to be linked to the metal atom by an ionic bond with little polarization. A dinitrogen complex can be considered to be a hybrid of two major resonance forms, $M-N^+ \equiv N$ and $M=N^+=N^-$. Because the nitrogen atom directly attached to the metal atom has a formal positive charge in both forms, we expect decreased electron density on this nitrogen atom and a correspondingly higher binding energy. The nitrogen 1s spectrum of trans-[Ru(N₂)Cl-(diars)₂] consists of two peaks; we assign the higher binding energy to the nitrogen atom directly attached to the ruthenium atom. Leigh et al.,¹ made

Table I. Nitrogen 1s binding energies for some transition metal complexes.

Compound	Nitrogen 1s binding energy, (eV)	Intensity ratio	Separation (eV)
NaN ₃	403.7, 399.3	1:2	4.4
Ni(N ₃)(NO)[P(C ₆ H ₅) ₂] ₂	403.8, 399.6	1:2	4.2
trans-[Ru(N ₃)Cl(diars) ₂]	403.9, 399.2	1:2	4.7
trans-[Co(N ₃) ₂ (diars) ₂]ClO ₄	403.2, 399.1	1:2	4.1
[Cu(N ₃)[P(C ₆ H ₅) ₃] ₂]	403.7, 399.2	1:2	4.5
[Rh(N ₃)(CO) ₂] ₂	403.2, 399.3	1:2	3.9
[As(C ₆ H ₅) ₄] ₂ [Fe(N ₃) ₅]	402.8, 398.7	1:2	4.1
trans-[Ru(N ₂)Cl(diars) ₂]	402.3, 400.7	1:1	1.6
Re(N ₂)Cl(diphos) ₂	399.9, 397.9	1:1	2.0
[C ₆ H ₅ (N ₂)]BF ₄	405.1, 403.8	1:1	1.3
K ₃ [Ru ₂ N(Cl) ₈ (H ₂ O) ₂]	399.8		
ReN(Cl) ₂ [P(C ₆ H ₅) ₃] ₂	398.8		

a similar assignment for [Re(N₂)Cl(diphos)₂].

The nitrogen 1s binding energies of K₃[Ru₂N(Cl)₈(H₂O)₂] and ReN(Cl)₂[P(C₆H₅)₃]₂ are of interest because these complexes contain nitride ion ligands that are bridging and nonbridging, respectively. In the former complex, two metal atoms compete for the electron density of the bridging nitride; therefore a higher binding energy is observed for this compound even though the complex has a 3- charge.

* Abstracted from Inorg. Chem. **11**, 1434 (1972).

1. G. J. Leigh, J. N. Murrell, W. Bremser and W. G. Proctor, J. Chem. Soc. D, 1661 (1970).

d. The Estimation of Core-Electron Binding-Energy Shifts Using the Concept of the Equivalence of Equally Charged Cores*

William L. Jolly

This review article summarizes the theory and applications of the "equivalent core" or "thermodynamic" method of estimating binding energy shifts. The predictive power of the method is demonstrated for gaseous compounds of boron, carbon, nitrogen, oxygen, and xenon, for gaseous monatomic ions of sulfur and chlorine, and for solid compounds of boron, carbon, nitrogen, and iodine. The use of the method for estimating chemical reaction energies from binding energy shifts is illustrated.

* Abstracted from a paper in Electron Spectroscopy, edited by D. A. Shirley (North-Holland, Amsterdam, 1972), pp. 629-645.

e. The Correlation of Core Binding Energies by a Potential Model Based on "Half-Ionized" Cores and a New Method for Calculating Atomic Charges*

William L. Jolly, Winfield B. Perry, and Gregory R. Andersen

If we make the approximation that the atoms of molecules are non-overlapping conducting spheres, we can estimate core electron binding energies from estimated atomic charges by using the relation

$$E_B = kQ + V + \lambda,$$

where Q is the charge of the atom which loses the core electron, V is the Coulomb potential energy of an electron at the hypothetical vacated site of that atom in the midst of the other atoms of the molecule, and k and λ are empirical constants. The energy V is calculated from the relation $V = \sum (q/r)$, in which q is the charge on an atom, r is its distance from the site of the atom vacancy, and the sum is carried out over all the atoms. Implicit in the equation is the assumption that the core binding energy is a function only of the initial state of the molecule. However, we know that during the time required for the ejection of a core electron from an atom in a molecule, the valence electrons of the molecule shift

toward the nucleus of the atom in which the core hole is created. This concurrent valence electron relaxation process is believed to be essentially complete in the time of the photoelectric process. Therefore, if we wish to calculate accurately the binding energy by a hypothetical "sudden" process in which the valence electrons are assumed to remain fixed, we cannot use the valence electron distribution of either the initial molecule or of the final core-hole ion. Use of the valence electron distribution of the initial molecule would yield a binding energy too high by the "relaxation energy"; use of the valence electron distribution of the final ion would yield a binding energy too low because of the concentration of negative charge around the core. However, some valence electron distribution between these two extremes, probably close to the average distribution, will give the right energy. We have developed a procedure for correlating and predicting core electron binding energies based on this data.

Using the above theory as a basis, we have devised a simple empirical method, involving electronegativity parameters, for estimating atomic charges. The method permits us to correlate 129 different binding energies (for compounds of boron, carbon, nitrogen, and fluorine) with an overall standard deviation of ± 0.61 eV.

* Abstracted from Faraday Disc. Chem. Soc., 54 (1972) and LBL-1417.

f. The Use of X-Ray Photoelectron Spectroscopy to Assess d Orbital Participation in Compounds of Silicon and Germanium*

Winfield B. Perry and William L. Jolly

Chemical shifts in core binding energies have been determined for analogous gaseous compounds of carbon, silicon, and germanium. These data, in conjunction with the atomic charge potential model and both CNDO/2 and electronegativity parameter charges, indicate that the silicon and germanium atoms in these compounds, except for SiH_4 and GeH_4 , have unexpectedly negative charges. The results are consistent with the existence of significant $\text{p}\pi\text{-d}\pi$ bonding in these compounds.

* Abstracted from Chem. Phys. Letters, 17, 611 (1972).

2. BORON HYDRIDE CHEMISTRY

a. A Kinetic Study of the Intermediates in the Hydrolysis of the Hydroborate Ion*

Francis T. Wang and William L. Jolly

The hydroborate ion (otherwise known as borohydride, tetrahydroborate, and tetrahydridoborate) undergoes hydrolysis in aqueous solutions to give boric acid below pH 9 and borate above pH 9.

A variety of experimental data have shown that the hydrolysis proceeds in four steps, with the intermediate formation of trihydro-, dihydro-, and monohydroboron species.

In the present study we have shown that the kinetics of the four consecutive steps of the acid hydrolysis of hydroborate can be separately studied by appropriate adjustments of the reaction temperatures and the hydrogen ion concentrations. We have prepared acidic solutions in which the monohydroboron intermediate was the only boron-hydrogen species present and solutions in which either the dihydro- or trihydroboron intermediate was the major boron-hydrogen species present. Solutions containing the species BH(OH)_3 , $\text{BH}_2(\text{OH})_2^-$, or BH_3OH^- were prepared by the addition of excess sodium hydroxide to acidic solutions containing the appropriate intermediates. The kinetics of the hydrolysis of these anions was studied.

The stepwise hydrolysis of hydroborate has been studied in cold 88:12 vol % methanol-water solutions in the hydrogen ion concentration range 0.1-1.1 M. At -78° , BH_4^- rapidly hydrolyzes to H_2OBH_3 , which, in turn, hydrolyzes to $\text{BH}_2(\text{H}_2\text{O})_2^+$ according to the rate equation $-d \ln [\text{H}_2\text{OBH}_3]/dt = 0.0015 \text{ sec}^{-1} + 0.0016[\text{H}^+] \text{ sec}^{-1} \text{ M}^{-1}$. The rate data for the hydrolysis of $\text{BH}_2(\text{H}_2\text{O})_2^+$ solutions at -36° are consistent with the following rapid equilibrium ($K = 6.4$): $\text{H}^+ + \text{H}_2\text{OBH}_2\text{OH} = \text{BH}_2(\text{H}_2\text{O})_2^+$. The $\text{BH}_2(\text{H}_2\text{O})_2^+$ ion is stable toward hydrolysis, whereas its conjugate base hydrolyzes to $\text{H}_2\text{OBH(OH)}_2$ according to the rate equation $-d \ln [\text{H}_2\text{OBH(OH)}_2]/dt = 0.017 \text{ sec}^{-1}$. At -36° , $\text{H}_2\text{OBH(OH)}_2$ hydrolyzes to B(OH)_3 according to the rate equation $-d \ln [\text{H}_2\text{OBH(OH)}_2]/dt = 3.3 \times 10^{-4} \text{ sec}^{-1}$. The species H_2OBH_3 , $\text{BH}_2(\text{H}_2\text{O})_2^+$, and

$\text{H}_2\text{OBH}(\text{OH})_2$ are converted to the anions BH_3OH^- , $\text{BH}_2(\text{OH})_2^-$, and $\text{BH}(\text{OH})_3^-$, respectively, by the addition of hydroxide. These anions undergo hydrolysis in nonbuffered, strongly alkaline solutions according to the rate equations $-d \ln [\text{BH}_3\text{OH}^-]/dt = 1.8 \times 10^{-4} \text{ sec}^{-1}$ at 20° ; $-d \ln [\text{BH}_2(\text{OH})_2^-]/dt = 2.2 \times 10^{-5} \text{ sec}^{-1}$ and $-d \ln [\text{BH}(\text{OH})_3^-]/dt = 1.1 \times 10^{-3} \text{ sec}^{-1}$ at 0° . The boron-11 NMR spectrum of BH_3OH^- is a 1:3:3:1 quartet, with $J_{\text{B-H}} = 87 \text{ Hz}$ centered 12 ppm upfield from the borate singlet.

* Abstracted from Inorg. Chem. 11, 1933 (1972).

b. The Asymmetric Cleavage of Diborane by Water. The Structure of Diborane Dihydrate*

Patricia A. Finn and William L. Jolly

The cleavage of the bridging hydrogen bonds in diborane by a Lewis base, X, can be either symmetric, to give BH_2X , or asymmetric, to give BH_2X_2^- and BH_4^- . In the reaction of ammonia with diborane, both types of cleavage have been observed. With increasing methyl substitution in the methylamine series, there is an increasing tendency for symmetric cleavage. Various ethers cleave diborane symmetrically, whereas dimethyl sulfoxide cleaves diborane asymmetrically. It appears that it is not yet possible to predict the course of such reactions with certainty.

In studies of the reaction of diborane with water and alcohols at room temperature, no intermediate cleavage products have been isolated because complete hydrolysis occurs rapidly. Davis and Gottbrath¹ were able to isolate sodium hydroborate from the reaction of diborane with aqueous sodium hydroxide at 0° , and Jolly and Schmitt² prepared potassium hydroborate by the reaction of diborane with powdered potassium hydroxide at -30° . These results are consistent with asymmetric cleavage of diborane and prompted a further study of this type of reaction. This paper describes the preparation and characterization of the initial diborane-water reaction product.

The dihydrate and diethanolate of diborane have been prepared at -130° and their compositions have been established by stoichiometric measurements. The dihydrate is assigned the structure $\text{BH}_2(\text{H}_2\text{O})_2\text{BH}_4^-$ on the basis of low-temperature infrared spectra of the deuterated and nondeuterated species. A study of the evolution of hydrogen from the reaction of diborane with a solution of HCl in a water-methanol mixture at -78° has provided further evidence for the

asymmetric cleavage of diborane by water and alcohol.

* Abstracted from Inorg. Chem. 11, 1941 (1972).

1. R. E. Davis and J. A. Gottbrath, Chem. Ind. (London), 1961 (1961); R. E. Davis and J. A. Gottbrath, Inorg. Chem. 4, 1512 (1965).
2. W. L. Jolly and T. Schmitt, J. Am. Chem. Soc. 83, 4282 (1966).

c. Preparation of the BH_3OH^- Ion with a "Quenching Flow Reactor"

Janice B. Reed and William L. Jolly

The work of Wang and Jolly¹ indicated that, in the room-temperature reaction of H^+ and BH_4^- , the intermediate H_2OBH_2 would be expected to have a lifetime of the order of magnitude of milliseconds. Therefore an apparatus was set up for mixing streams of H^+ and BH_4^- solutions and then quickly mixing the resulting reaction mixture with a stream of OH^- solution. With this apparatus we have prepared BH_3OH^- solutions, free of other borohydride species, at concentrations as high as 0.21 M in 21% yield and 0.052 M in 52% yield. Kinetic data for the hydrolysis of the BH_3OH^- at 20° yield a half-life of 4.1 hours. We plan to investigate the chemical properties of the BH_3OH^- species. With this technique it should be possible to prepare, by use of slower quenching, the other borohydride intermediates, $\text{BH}_2(\text{OH})_2^-$ and $\text{BH}(\text{OH})_3^-$.

The general utility of the quenching method has been demonstrated² by preparing the peroxyxynitrite ion (OONO^-) in 72% yield from H_2O_2 and NO_2^- . In this synthesis, the very unstable HOONO is prepared from H_2O_2 and HNO_2 , and it is then quenched with OH^- which converts it to the relatively stable OONO^- . Further development of this synthesis is planned.

1. F. T. Wang and W. L. Jolly, Inorg. Chem. 11, 1933 (1972).
2. Work carried out by Mr. H. H. Ho in Chemistry 106, Fall, 1972.

3. SULFUR-NITROGEN CHEMISTRY

a. The Reaction of Heptasulfur Imide and Diborane*

Marshall H. Mendelsohn and William L. Jolly

It is known that heptasulfur imide reacts

with boron trichloride and boron tribromide to give S_7NBCl_2 and S_7NBBR_2 , respectively. In this note we report the results of our study of the reaction of heptasulfur imide with diborane. This study was undertaken to determine whether the reaction gives an analogous product (S_7NBH_2), a borane adduct ($S_7NH \cdot BH_3$), or a diborane derivative such as $S_7NB_2H_5$.

The reaction of heptasulfur imide with diborane was carried out in various ether solvents, at either room temperature or 0° . The experimental results show that, with diborane in excess, 0.5 mol of diborane reacts per mole of S_7NH and that 1 mol of hydrogen is formed per mole of S_7NH . This stoichiometry corresponds to the reaction $S_7NH + 0.5B_2H_6 \rightarrow S_7NBH_2 + H_2$.

When the reaction is carried out in diethyl ether at 0° , some of the product precipitates as a white, crystalline ether adduct, $S_7NBH_2 \cdot Et_2O$. Similar adducts can be obtained from the other ethers by vacuum evaporation of the solvent and removal of excess diborane. The compounds undergo rapid hydrolysis with excess water at room temperature: $S_7NBH_2 \cdot \text{ether} + 3H_2O \rightarrow S_7NH + B(OH)_3 + 2H_2 + \text{ether}$.

The ^{11}B NMR spectrum of S_7NBH_2 in diethyl ether solution consists of a 1:2:1 triplet due to coupling with the two protons of the BH_2 group. The Raman spectrum of the diethyl ether adduct has lines at 2419 and 2409 cm^{-1} , characteristic of terminal BH_2 groups, and lines at 766 and 750 cm^{-1} , typical S-N stretching frequencies.

The only products that were stable (as determined by hydrogen evolution) were those obtained from diethyl ether and tetrahydrofuran. The diethyl ether adduct is stable at room temperature in the absence of air and moisture, and the product from tetrahydrofuran is stable at 0° . Hydrogen, hydrogen sulfide, and ether were identified as decomposition products of the tetrahydrofuran and monoglyme adducts at room temperature.

A white solid pyridine adduct, $S_7NBH_2 \cdot C_5H_5N$, was isolated from the reaction of $S_7NBH_2 \cdot Et_2O$ with pyridine. Pure samples of this compound were stable indefinitely *in vacuo* at 0° and could be kept in an ordinary closed bottle at room temperature for as long as 5 days without decomposition. However, impure samples decomposed within 1 or 2 days.

When the reaction of heptasulfur imide and diborane is carried out with an excess of

S_7NH in tetrahydrofuran at 0° , the reaction does not stop with the formation of S_7NBH_2 , as evidenced by the continued slow evolution of hydrogen. Presumably the following subsequent reaction occurs:

However, the reaction was incomplete after one month and was not further studied.

* Abstracted from Inorg. Chem. 11, 1944 (1972).

b. The Structures of Sulfur-Nitrogen Compounds*

William L. Jolly

In this paper the structures of compounds which contain rings or chains of alternating sulfur and nitrogen atoms are discussed. During the last 15 years or so this class of compounds has frustrated and mystified chemists because various structure determinations have often showed that structures which had been predicted for these compounds were wrong. However, enough structures of such compounds are now known that it is possible to systematize and rationalize the data.

The structures and bonding of the following species have been studied: S_2N_2 , $S_2N_2^+$, $S_2N_2^{2+}$, $S_3N_3Cl_3$, $S_3N_3O_3Cl_3$, S_7NH , $S_6(NH)_2$, $S_5(NH)_3$, $S_4N_4H_4$, $S_4N_4F_4$, $S_4N_4^{2-}$, S_4N_4 , $S_4N_4^{2+}$, S_5N_5 , $S_3N_2O_2$, S_3N_2Cl , $S_3N_3NPPH_3$, S_4N_2 , and $S_4N_3^+$. These species are characterized by rings or chains of alternating sulfur and nitrogen atoms. The structures are rationalized by comparison with isoelectronic compounds of known structure and by assuming delocalized π bonding whenever possible.

* Abstracted from Advances in Chemistry Series 110, 92 (1972).

4. THE PREDICTION OF GAS-PHASE LEWIS ACID-BASE DISSOCIATION HEATS WITH AN EMPIRICAL FOUR-PARAMETER EQUATION*

William L. Jolly, John D. Illige, and Marshall H. Mendelsohn

In 1952, Mulliken¹ showed theoretically that the dissociation energy of a Lewis acid-base adduct can be partitioned into a "no-bond" part and a "dative" or covalent part. In 1954, Edwards² showed that the free energies (or logarithms of equilibrium constants) of Lewis acid-base reactions can be reproduced by the two-term four-parameter

equation

$$\log \frac{K}{K_0} = \alpha E_n + \beta H,$$

where K is the equilibrium constant for the reaction of a base with a particular acid and K_0 is the constant for the corresponding reaction of a reference base. The parameters α and β are empirical constants characteristic of the acid, and E_n and H are independent parameters for the base. More recently, Drago and Wayland⁵ used a similar equation to reproduce the heats of dissociation of Lewis acid-base adducts:

$$\Delta H = E_A E_B + C_A C_B.$$

Two empirical parameters, E_A and C_A , were assigned to each acid, and two empirical parameters, E_B and C_B , were assigned to each base. The $E_A E_B$ term was interpreted as a measure of electrostatic interaction energy, and the $C_A C_B$ term was interpreted as a measure of covalent bond energy. By application of the equation to reactions of neutral acids and bases in the gas state or in poorly solvating solvents (for which the dissociation heats ranged from 0.5 to 18.0 kcal/mol), it was possible to correlate the dissociation heats with an average error of approximately ± 0.1 kcal/mol.

Dissociation heats are available for an extensive set of gaseous compounds, not considered by Drago and Wayland, which may be considered as Lewis acid-base adducts. Most of these compounds are adducts of cationic acids and anionic bases.

By use of the empirically evaluated parameters for 14 acids and 12 bases, the heats of 105 different dissociations are reproduced with an average error of ± 3.9 kcal/mol. The method gives poor results for adducts in which the dissociated bonds are either weakened by lone-pair repulsions or affected by unusual π -bonding effects.

* Abstracted from Inorg. Chem. **11**, 869 (1972).

1. R. S. Mulliken, J. Am. Chem. Soc. **74**, 811 (1952).
2. J. O. Edwards, *ibid.*, **76**, 1540 (1954); **78**, 1819 (1956).
3. R. S. Drago and B. B. Wayland, *ibid.*, **87**, 3571 (1965).

5. RESEARCH PLANS FOR CALENDAR YEAR 1973

William L. Jolly

a. X-Ray Photoelectron Spectroscopy

We shall try to devise a method for obtaining the spectra of high temperature gaseous species. The main problem to be overcome is the effusion of vapor through the electron slit, and consequent fouling of the vacuum chamber. The use of a beam or jet of vapor molecules seems indicated.

We plan to investigate the binding energy shifts for compounds of nickel and iron in various oxidation states in order to determine the valence electron distribution in these compounds.

We are developing a new method for calculating molecular electron distributions, based on electronegativity equalization.

b. Boron Hydride Chemistry

We shall exploit the quenching flow reactor as far as possible. Good syntheses of $BH_2(OH)_2^-$ and $BH(OH)_3^-$ should be possible, as well as non-boron-containing species such as OOO^- .

c. Sulfur-Nitrogen Chemistry

We hope to study quantitatively the isomerization of the S_7N^- ion in ether solution (see Section 4-a) by means of UV and visible spectrophotometry. An apparatus has been built for preparing the solutions and transferring them to an absorption cell in the complete absence of air. We plan to study the spectrum as a function of concentration and temperature.

6. 1972 PUBLICATIONS AND REPORTS

William L. Jolly and Associates

Journals and books

1. William L. Jolly, The Structures of Sulfur-Nitrogen Compounds, in Advances in Chemistry Series 110, 92 (1972).
2. William L. Jolly, The Estimation of Core-Electron Binding-Energy Shifts Using the Concept of the Equivalence of Equally Charged Cores, in Electron Spectroscopy, edited by D. A. Shirley (North-Holland, Amsterdam, 1972), pp. 629-645.

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13. Winfield B. Perry and William L. Jolly, The Use of X-Ray Photoelectron Spectroscopy to Assess d Orbital Participation in Compounds of Silicon and Germanium, *Chem. Phys. Letters* 17, 611 (1972).
2. William L. Jolly, X-Ray Photoelectron Spectroscopy and Intermediates in the Hydrolysis of Borohydride and Diborane, A. C. S. Visiting Scientist Program, California State Polytechnic College, Pomona, Calif., Feb. 16-17, 1972, and University of Nevada, Reno, March 23-24, 1972.
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5. W. L. Jolly, Inorganic Applications of Photoelectron Spectroscopy, Gordon Research Conference on High Temperature Chemistry, Andover, N. H., August 7-11, 1972.
6. W. L. Jolly, X-Ray Photoelectron Spectroscopy, University of Glasgow, Glasgow, Scotland, September 5, 1972, and University of Edinburgh, Edinburgh, Scotland, September 7, 1972.
7. W. L. Jolly, The Correlation of Core Binding Energies by a Potential Model Based on "Half-Ionized" Cores and a New Method for Calculating Atomic Charges, Faraday Discussion of the Chemical Society, Brighton, England, September 12-14, 1972.
8. W. L. Jolly, X-Ray Photoelectron Spectroscopy, Frontiers in Chemistry Lecture, Wayne State University, Detroit, Mich., October 30, 1972.
9. W. L. Jolly, The Estimation of Atomic Charges in Molecules, University of Windsor, Windsor, Ontario, Canada, October 31, 1972.
10. W. L. Jolly, X-Ray Photoelectron Spectroscopy, The Estimation of Atomic Charges in Molecules, Intermediates in the Hydrolysis of Borohydride and Diborane, and A Comparison of Analogous Hydride Derivatives of Germanium and Carbon, presented during Visiting Professorship at the University of Western Ontario, London, Canada, November 7-16, 1972.

Papers presented

1. W. L. Jolly, Thermochemical Estimates of Core-Level Binding Energy Shifts, Symposium on Electron Spectroscopy, Case Western Reserve University, Cleveland, Ohio, January 10-11, 1972.
11. W. L. Jolly, Chemical Shifts in Core Electron Binding Energies, Symposium on Photoelectron Spectroscopy, Yale University, New Haven, Conn., November 30, 1972.

LBL report

1. Marshall H. Mendelsohn and William L. Jolly, Reactions of the Heptasulfur Imide Anion, submitted to J. Inorg. Nucl. Chem. (LBL-820, August 1972).

2. E. R. Staricco, C. Riddle, and William L. Jolly, The Reaction of Potassium Germyl with Boron Trimethyl, submitted to J. Inorg. Nucl. Chem. (LBL-826, April 1972).

3. William L. Jolly, W. B. Perry, and G. Anderson, A Method for Estimating Atomic Charges Based on Electronegativity Parameters, LBL-1417, December 1972.

Robert E. Connick, Principal Investigator

1. OXYGEN-17 NMR STUDY OF THE RATE OF WATER EXCHANGE FROM PARTIALLY COMPLEXED NICKEL ION

Thomas V. Rowland

In a continuing study of the exchange lifetimes of water molecules in the first coordination spheres of metal ions, partially complexed nickel ion is being investigated. The 1:1 complex with iminodiacetate ion has three positions occupied by water molecules, two of which are equivalent. Measurements of the line width of the oxygen-17 bulk water resonance are being made as a function of temperature to determine the effect of complexing on the water exchange rate and to see if the two kinds of coordinated water molecules exchange at appreciably different rates. The measurements have also revealed an unexpected line broadening near 0°C which is being investigated.

2. ¹⁷O-NMR STUDIES OF WATER MOLECULES IN THE SECOND COORDINATION SPHERE OF Cr³⁺

William L. Earl

Olson, Kawagawa, and Taube [J. Chem. Phys. 51, 289 (1969)] have used the line broadening of ¹⁷O of bulk water in solutions of Cr(III) to set a limit on the lifetime of water molecules in the second coordination sphere of Cr(III). The present work is directed towards fixing the value of the lifetime by combining both transverse and longitudinal relaxation times for the ¹⁷O. A preliminary value of 3×10^{-10} sec for the lifetime at 25° is being refined. These results will give the first measurement of the exchange lifetime for a second coordination sphere water molecule, a result of which is of interest in the understanding of mechanisms and rates in aqueous solutions.

3. COMPUTER SIMULATION OF SOLVENT EXCHANGE FROM THE FIRST COORDINATION SPHERES OF METAL IONS

Robert E. Connick

In order to understand better the complex movements of the many particles involved in the exchange of a first coordination sphere water molecule on a metal ion with the bulk water, computer calculations of simplified

models are being undertaken. So far only two-dimensional cases with 72 particles have been attempted. Single-step and three-step square wells have been calculated for a single radius. An 18-step well will be tried next and the variation of rate and reaction path with depth of well and radius of "metal ion" will be studied before going to three dimensions. It is hoped that the calculations will give information on the mechanism of exchange and the effect of radius and charge of the "metal ion." The work is being done in collaboration with Dr. Berni Alder of the Livermore Laboratory.

4. RAMAN SPECTRUM OF TRIIODIDE ION

Kenneth Suslick

It is reported in the literature [Maki and Forneris, Spectrochim. Acta 23A, 867 (1967)] that triiodide ion in aqueous solution shows two Raman lines, which would require an unsymmetrical structure. With the availability of laser Raman apparatus such measurements can be made much more precisely. The present study showed that in I₃⁻ solutions containing excess I⁻ there are indeed two lines, but the intensity of one of these is a function of the I⁻ concentration, disappearing at low iodide. Therefore, the Raman data do not give evidence of an unsymmetrical structure for triiodide ion. The line which varied with iodide concentration probably arises from the presence of appreciable I₄²⁻ in the solutions.

5. RESEARCH PLANS FOR CALENDAR YEAR 1973

Robert E. Connick

The studies of water exchange rates for the first coordination sphere of metal ions will be continued, and it is hoped that several of the simple hydrated metal ions whose rates are very fast can be measured. Water exchange on additional partially complexed ions will be investigated. The computer modeling of the exchange process will be extended to three dimensions.

6. 1972 PUBLICATIONS AND REPORTS

Robert E. Connick and Associates

Journal

1. James W. Neely and Robert E. Connick, Oxygen-17 Nuclear Magnetic Resonance Studies of Aqueous Nickel Ion, J. Am. Chem. Soc. 94, 3419 (1972).

LBL Reports

1. E. E. Genser and R. E. Connick, The Exchange of Iodide Ion with Triiodide ion Studied by Nuclear Magnetic Resonance, LBL-869, July 1972.

Neil Bartlett, Principal Investigator

1. NOBLE-GAS AND HALOGEN CHEMISTRY

a. Krypton Chemistry

Douglas E. McKee and Neil Bartlett

The more effective synthesis of KrF_2 via the 10 MeV proton bombardment of Kr/F_2 mixtures has made for a significant advance of KrF_2 chemistry this year. The KrF^+ salt $\text{KrF}^+\text{Sb}_2\text{F}_{11}^-$ has been used to oxidize XeOF_4 to XeOF_5^+ :

* Abstracted from D. E. McKee, C. J. Adams, and Neil Bartlett, Chem. Comm., January issue 1973.

b. Xenon Chemistry

Christopher J. Adams, Donald D. Gibling, Kevin Leary, Douglas E. McKee, Boris Zemva, Thomas J. Richardson and Neil Bartlett

(i) Xenon(II) Chemistry (Zemva): Interaction of XeF_2 with PdF_4 yields PdF_4 complexes of which: $3\text{XeF}_2 \cdot \text{PdF}_4$, $\text{XeF}_2 \cdot \text{PdF}_4$, $\text{XeF}_2 \cdot 2\text{PdF}_4$ are certain and $4\text{XeF}_2 \cdot \text{PdF}_4$ and $2\text{XeF}_2 \cdot \text{PdF}_4$ possible.

(T. Richardson): The hydrolysis of $\text{Xe}_2\text{F}_3^+\text{RuF}_6^-$ yields almost a 100% yield of RuO_4 , suggesting that the hydrolysis of Xe(II) fluoro-species may be an effective way to

Fig. 1(a). The structural unit $\text{XeF}_3^+\text{Sb}_2\text{F}_{11}^-$.
(XBL 729-6975)

Fig. 1(b). Stereogram showing the arrangement of the $\text{XeF}_3^+\text{Sb}_2\text{F}_{11}^-$ structural units within the unit cell--view along b.
(XBL 729-6983)

Fig. 1(c). The XeF_3^+ ion and its close contact with the $\text{Sb}_2\text{F}_{11}^-$ ion.
(XBL 729-6918)

prepare higher oxides. Hydrolysis of $\text{Xe}_2\text{F}_3^+\text{IrF}_6^-$ produces some volatile iridium species but so far IrO_4 has not been confirmed.

(ii) Xenon(IV) Compounds*: The XeF_3^+ salts $\text{XeF}_3^+\text{SbF}_6^-$ and $\text{XeF}_3^+\text{Sb}_2\text{F}_{11}^-$ have been prepared (McKee) and characterized by Raman spectroscopy (Adams). A full crystal structure determination (McKee with Zalkin) of the $\text{XeF}_3^+\text{Sb}_2\text{F}_{11}^-$ has been carried out* and is shown as Fig. 1.

(iii) Xenon(VI) Compounds: The salts $[\text{XeF}_5^+]_2\text{PdF}_6^{2-}$, $[\text{Xe}_2\text{F}_{11}^+]_2\text{PdF}_6^{2-}$, $\text{XeF}_5^+\text{AuF}_6^-$

and $\text{Xe}_2\text{F}_{11}^+\text{AuF}_6^-$ have been prepared and characterized by Raman spectroscopy (Leary). The crystal structures of the first and the last have been determined. The $[\text{XeF}_5^+]_2\text{PdF}_6^{2-}$ structure is represented in Fig. 2. The cations and anions are associated in 'rings' containing 2XeF_5^+ and 2PdF_6^{2-} (the anions are shared between two 'rings'). These 'rings' are almost identical to those seen in $\text{XeF}_5^+\text{AsF}_6^-$ (LBL-670, Ph.D. thesis, F. Hollander). The XeF_5^+ species, although essentially the same as in $\text{XeF}_5^+\text{RuF}_6^-$ (1971 Annual Report), are coordinated to 3 F ligands of the anions, whereas in $\text{XeF}_5^+\text{RuF}_6^-$ the cation coordination to other anion ligands is 4.

The preparation of $\text{Xe}_2\text{F}_{11}^+\text{AuF}_6^-$ (Leary) is especially noteworthy since it represents the first Au(V) compound.* The crystal structure

Fig. 2(a). The formula unit in $[\text{XeF}_5^+]_2\text{PdF}_6^{2-}$.

(XBL 724-6188)

Fig. 2(b). Stereogram of the $\text{XeF}_5^+\text{AsF}_6^{2-}$ rings in $[\text{XeF}_5^+]_2\text{PdF}_6^{2-}$.

(XBL 724-6130)

Anion		Cation			
F3-Xe-F3'	179.1(2)*	F1-Xe1-F2	79.6(4)*	F4-Xe2-F8	79.4(4)*
F8	90.4(4)	F3	79.0(4)	F5	81.1(6)
F3-Xe-F11	91.6(4)	F2-Xe1-F2	86.0(3)	F6-Xe2-F6	86.6(3)
F12	88.0(5)	F3	87.1(4)	F5	87.4(6)
F10-Xe-F11	89.2(5)	F3-Xe1-F3	91.1(3)	F5-Xe2-F5	89.9(3)
F12	91.2(6)	Xe2-F7-Xe1	189.2(2)		
Interatomic Distances and Angles					
Xe1-F8	2.64(1) Å	F1-Xe1-F7	147.4(8)*	F4-Xe2-F7	146.3(7)*
F8	3.27(1)	F8	136.3(6)	F12	139.8(7)
Xe2-F12	2.64(1)	F9	152.2(5)	F9	136.9(2)
F9	3.52(1)

Fig. 3. The structural unit of $\text{Xe}_2\text{F}_{11}^+\text{AuF}_6^-$ (estimated standard deviations in parentheses). (XBL 7210-7119)

of the compound not only structurally defines the AuF_6^- ion for the first time but also establishes the geometry of the $\text{Xe}_2\text{F}_{11}^+$ ion. The structure is shown in Fig. 3.

The cation $\text{Xe}_2\text{F}_{11}^+$ is very like two XeF_5^+ groups joined by an F^- . The short Xe-F bridging distance of approximately 2.2 Å indicates, however, that there is some covalency in the interaction. The complex cation is probably best described as a resonance hybrid of $(\text{XeF}_5^+\text{F}^-\text{XeF}_5^+)$, $(\text{XeF}_6\text{XeF}_5^+)$, and $(\text{XeF}_5^+\text{XeF}_6)$ canonical forms, with the first form dominating.

The Raman spectra of the AuF_6^- and PdF_6^{2-} salts of $\text{Xe}_2\text{F}_{11}^+$ and XeF_5^+ given in Table 6¹ show the clear relationship of $\text{Xe}_2\text{F}_{11}^+$ to XeF_5^+ . The XeF_5^+ has been further defined vibrationally (Adams). Comparison with data for isoelectronic molecules reveals unusual vibrational properties for XeF_5^+ , in that the symmetric stretching fundamentals lie lower than in IF_5 , though the bond lengths of XeF_5^+ are the shorter. The probable reason lies with ligand-ligand repulsions in the crowded XeF_5^+ molecule, and this should be evident in the values for interaction constants given by a full normal coordinate analysis. A similar

TABLE I

Raman Spectra of $\text{Xe}_2\text{F}_{11}^+$ Salts and Related Species (shifts in cm^{-1})

IF_5 (a)	$(\text{NO}^+)_2\text{PdF}_6^{2-}$	$(\text{XeF}_5^+)_2\text{PdF}_6^{2-}$	$(\text{Xe}_2\text{F}_{11}^+)_2\text{PdF}_6^{2-}$	$(\text{Xe}_2\text{F}_{11}^+)\text{AuF}_6^-$	$\text{Cs}^+\text{AuF}_6^-$
710(ν_1) vs	653 s	668 w	651 vs	661 s	
631(ν_2) sh	634 vw	630 m	640 w		
614(ν_2) vs	616 vw	615 w	610 m	626 w	
	606 w	606 w	600 s		
602(ν_4) sh	590 ms	591 s	595 vs	595(ν_1) vs	
		583 m	590 vs		
573(ν_1) s	558 ms	568 s			
554(ν_2) ms	535 s	546 w			
				530(ν_2) vw	
370(ν_3) w	425 vw	412 vw	396 vw	400 w	
	396 vw	375 w	356 w		
318(ν_3) m	309 w	296 w (b)	290 w		
274(ν_6) w	269 w	270 w (b)	---		
243(ν_5) ms	245 w	245 w (b)			
				221 m	224(ν_5) s

(a) L. E. Alexander and I. R. Beattie, *J. Chem. Soc. (A)*, 1971, 3091.

Table II

Raman and Infrared Spectra of the Tetrafluoroiodate[III]

Bu ⁿ ₄ NIF ₄		XeF ₄ ^(a)		Assignment in D _{4h} symmetry
Solid	Solu. in MeCN	gas		
R	r lr	R	lr	
511,s	519,s,p	554.3		1(a _{1g}) MF ₄ in-phase str.
			291	2(a _{2u}) MF ₄ out-of-plane bend
199w	200vw	218		3(b _{1g}) MF ₄ in-plane scissor
452m	460w,dp	524		5(b _{2g}) MF ₄ out-of-phase str.
	475s		586	6(e _g) MF ₄ degenerate str.

(a) P. Tsao, C. C. Cobb, and H. H. Claassen, J. Chem. Phys. **54**, 5247 (1971).

effect has been observed for the series SbF₆⁻, TeF₆, IF₆⁺. These and related studies promise to throw light on the problem of structure and bonding in XeF₆ itself.

The synthesis of Xe₂F₁₁⁺AuF₆⁻ points to properties of XeF₆ which have not been exploited previously. The hexafluoride is not oxidizable and melts at the relatively low temperature of 49.5°C. It is also a moderately good base. It is, therefore, valuable as solvent and base in promoting unusually high oxidation states of the elements (see Research Plans for 1973).

The XeOF₃⁺ salts, XeOF₃⁺SbF₆⁻ and XeOF₃⁺Sb₂F₁₁⁻ have been prepared^{**} (McKee), and Raman studies (McKee and Adams) have demonstrated the salt formulations.

* K. Leary and N. Bartlett, J. Chem. Soc. Chem. Comm. 903 (1972).

** D. E. McKee, C. J. Adams, and N. Bartlett, J. Chem. Soc. Chem. Comm. 26 (1973).

c. Halogen Chemistry

(i) Iodine Fluoranes (Adams):

IF₄⁻ - Buⁿ₄NIF₄ was prepared by the reduction of IF₅ with Buⁿ₄NI. Infrared and Raman data showed the anion to be square planar, and thus isostructural with XeF₄ (Table II). IF₈⁻ - IF₇ is a much weaker Lewis acid than XeF₆; direct reaction with alkali metal fluorides is hampered by its poor solvent properties. Attempts to prepare octafluoroiodates (VII) centered on the reaction of NOF and IF₇, which

combine together in the vapor phase to give a white solid, composition NOF·IF₇, with a vapor pressure of ~ 300 mm at room temperature, the Raman spectrum of the solid at ca. -80°C shows a line at 2240 cm⁻¹ attributable to NO⁺, and a characteristic pattern of lines in the I-F stretching region. Reaction of this compound with cesium fluoride at -78°C in excess NOF as solvent produces a cesium fluoroiodate(VII), contaminated with CsNO₃ and residual CsF. The Raman spectrum of CsIF₈ in the I-F stretching region closely resembles NOF·IF₇. On the basis of the spectroscopic evidence the solid is believed to be predominantly CsIF₈, and efforts will be made to obtain its crystal structure.

(ii) IF₄⁺ (Gibler), has been shown to C_{2v} symmetry in the salt IF₄⁺SbF₆⁻ which is orthorhombic [a = 8.29(1), b = 8.34(1), c = 10.34(1)] and not tetragonal as had been thought previously.

2. FLUORIDES, OXYFLUORIDES, AND OXIDES OF THE TRANSITION METALS

Alain R. Tressaud, Kevin Leary, and Neil Bartlett

a. Fluorides of Rhodium and Iridium (Tressaud)

No noble-metal tetrafluoride crystal structure is presently known. The tetrafluoride of iridium has been established and magnetic studies (from 4°K to room temperature) have confirmed the low spin d⁵ system consistent with iridium(IV). Some subtle antiferromagnetic-like coupling shows up below 90°K.

Attempts to grow single crystals of IrF_4 by recrystallization from IrF_5 have failed, but good quality powder data support the relationship to the ThCl_4 unit cell. The body-centered pseudo monoclinic unit cell (true unit cell F orthorhombic) has $a = 6.680$, $b = 5.672$, $c = 6.680$ (all ± 0.003 Å), $\beta = 92.67^\circ$.

Since IrF_4 , PtF_4 , and PdF_4 are isomorphous they may well be isostructural and since the powder data indicate a similarity to the ThCl_4 (UCl_4) data there is the possibility of that type of structure occurring in these fluorides. Since the hexafluoride, pentafluoride, and trifluoride of iridium all show octahedral coordination of the metal atom, the adoption of the ThCl_4 structure (where Th is light-coordinated in chlorine) is unexpected.

Rhodium tetrafluoride is not isomorphous with the form of IrF_4 which is stable at room temperature; nor is RhF_4 isomorphous with RuF_4 .

Suitable single crystals of RhF_5 have been obtained for X-ray structure analysis and a high-precision structure has been obtained. (Fig. 1) This establishes that RhF_5 is isostructural with RuF_5 and OsF_5 but, for the first time, the precision permits meaningful discussion of the bonding. As may be seen from Fig. 1, the Rh-F-Rh bridge bonds (~ 2.0 Å) are significantly longer than the non-bridging (1.8 Å). This is consistent with single-electron Rh-F (bridge) bonds and electron-pair bonds for the uniquely bound F

ligands. The F atom packing in the $(\text{RhF}_5)_4$ structure is essentially hexagonal-close-packing. The Rh-F-Rh bridge angles of $\sim 136^\circ$ indicate considerable covalency in the bonding and represent the greatest possible departure from linearity allowable, without gross distortion of the RhF_5 units.

3. RESEARCH PLANS FOR CALENDAR YEAR 1973

Neil Bartlett

Noble-Gas and Related Chemistry. KrF^+ promises to be an oxidizer of extraordinary power. The possibility exists of ClF_6^+ , BrF_6^+ syntheses and transition element oxidations to previously unknown oxidation states.

Efforts will be made to isolate single crystals of an XeOF_5^+ salt so that the cation can be properly characterized. The related base XeOF_6 will be sought.

Raman studies of XeF_6 in a variety of solvents (HF , WF_6 , etc.) will be undertaken in order to better define the relationship of molecular XeF_6 to $\text{Xe}_2\text{F}_{11}^+$ and XeF_5^+ . XeF_6 will be further exploited as a solvent and base (see below).

The interaction of XeF_2 with XeF_3^+ and XeF_5^+ will be further investigated with regard to the F^- donor properties (and investigated with regard to the F^- donor properties (and bonding) in the xenon fluorides.

Efforts will be made to isolate salts of $\text{Xe}_3\text{F}_4^{2+}$. Synthesis of new Xe(II) compounds of formulae FXeR , or XeR_2 (where $\text{R} = \text{SF}_5$, OSF_5 , etc.) will be attempted. To this end the synthesis and properties of SF_5Br will be explored.

The interaction of XeF_2 and its salts with water will be exploited as an oxygen atom source, and species such as IrO_4 , IrOF_5 , OsO_2F_4 , OsF_5 will be sought. The crystal structure of CsIrF_8 (or a relative) will be attempted.

Transition, Lanthanide, and Actinide Fluorides and Oxyfluorides. Xenon hexafluoride-fluorine mixtures will be used to attempt the preparation of Np(VII), Pu(VIII), and Pr(V) salts.

The isolation of AuF_5 will be undertaken and the synthesis of AuF_6 will be attempted. The synthesis of AuF_6 would provide a more powerful oxidizer than PtF_6 . AuF_6 may oxidize

Fig. 1. The RhF₅ tetramer. (XBL 728-6758)

Kr spontaneously at ordinary temperatures and pressures. It is also conceivable that it could stabilize the ArF^+ ion in the salt $\text{ArF}^+ \text{AuF}_6^-$.

Hopefully the XeF_2 hydrolysis studies will provide a convenient synthetic route to higher oxide and oxyfluorides, but more traditional oxyfluorinations will also be undertaken in an effort to prepare NpOF_5 etc.

Single crystal and Raman studies of OsO_3F_2 will be undertaken to establish that the compound is a fluorine bridged polymer. Similar studies will be carried out with ReO_2F_3 .

PdF_4 and its xenon fluoride adducts will be further studied in an effort to prepare $\text{Xe}_3\text{F}_4^{++}$ salts and $\text{XeF}_5^+ \cdot \text{XeF}_2$ adducts and to obtain a crystal structure of PdF_4 .

4. 1972 PUBLICATIONS AND REPORTS

Neil Bartlett and Associates

Journals

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2. K. Leary and N. Bartlett, A New Oxidation State of Gold: The Preparation and Some Properties of $[\text{AuF}_6]^-$ Salts, *Chem. Comm.* 903 (1972) (LBL-870).
3. Neil Bartlett, Noble-Gas Compounds, *Endeavour* **XXIX** [114], 107 (1972) (LBL-834).
4. D. D. Gibling, C. J. Adams, M. Fischer, A. Zalkin, and N. Bartlett, Structural Studies of Trifluorosulfur(IV)yl, $[\text{SF}_3]^+$, Salts Including the Crystal Structure of $[\text{SF}_3]^+ [\text{BF}_4]^-$, *Inorg. Chem.* **11**, 2325 (1972) (LBL-469).
5. M. Wechsberg, P. A. Bulliner, F. O. Sladky, R. Mews, and N. Bartlett, Fluorosulfates and Perchlorates of Xenon(II) and the Salt $[(\text{FXeO})_2\text{S}(\text{O})\text{F}]^+ [\text{AsF}_6]^-$, *Inorg. Chem.* **11**, 3063 (1972) (LBL-168).
6. N. Bartlett, Noble-Gas Chemistry and Its Significance, *Jahrbuch der Akademie der Wissenschaften in Göttingen*, 1971, Vandenhoeck and Ruprecht, Göttingen, Germany (Dannie-Heineman Prize Address), (*Akademie-Jahrbuch*) (LBL-416).

Papers presented

1. N. Bartlett, "Bonding in Noble-Gas Chemistry," Simon Fraser University, March 28, 1972; Oregon State University, March 29, 1972; University of California, San Diego, June 13, 1972; University of Southern California, December 1, 1972.
2. N. Bartlett, European speaking tour: "The Highest Attainable Oxidation States of the Noble-Metals," University of Bordeaux, June 26, 1972; "Bonding in Noble-Gas Compounds," Jozef Stefan Institute, Ljubljana, Yugoslavia, June 27, 1972; "Bonding in Noble-Gas Compounds," Lehrstuhl B für Anorganische Chemie der Technische Universität, Braunschweig, Germany, July 1, 1972; "The Highest Attainable Oxidation States of the Elements," Anorganisch-Chemisches Institut der Universität, Göttingen, Germany, July 5, 1972; "Fluoride Bridge Bonding" and "Bonding in Noble-Gas Compounds," Institut für Anorganische und Analytische Chemie, Justus Liebig-Universität, Giessen, Germany, July 7, 1972; "Fluoride Bridge Bonding," Universität des Saarlandes, Saarbrücken, Germany, July 10, 1972; "Fluoride Bridge Bonding," Universität Dortmund, Dortmund, Germany, July 12, 1972; Bonding in Noble Gas Compounds," Institut für Anorganische Chemie der Technischen Hochschule Aachen, Aachen, Germany, July 14, 1972.
3. N. Bartlett, "Noble-Gas and Related Chemistry," 14th Annual Summer Conference of the California Association of Chemistry Teachers, Asilomar, California, August 25, 1972.
4. N. Bartlett, C. J. Adams, K. Leary, and D. E. McKee, "Acid-Base Properties of XeF_4 and XeOF_4 ," Annual ACS Meeting, New York, August 29, 1972.
5. N. Bartlett, "Concerning the Nature of the Bonding in Noble-Gas and Related Compounds," Plenary Lecture, Dalton Division Symposium, Autumn Meeting of the Chemical Society, Nottingham, England, September 26, 1972.
6. N. Bartlett, "Concerning the Nature of Bonding in Noble-Gas Compounds," ACPS Pacific Regional Meeting, Jack Tarr Hotel, San Francisco, October 16, 1972.

LBL reports

1. N. Bartlett, M. Gennis, D. D. Gibling, B. K. Morrell, and A. Zalkin, The Crystal Structures of $[\text{XeF}_5]^+ [\text{RuF}_6]^-$ and $[\text{XeF}_5]^+ [\text{RuF}_6]^-$, LBL-850, August 1972.

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3. D. E. McKee, A. Zalkin, and N. Bartlett, The Crystal Structure of $[\text{XeF}_3]^+[\text{Sb}_2\text{F}_{11}]^-$, LBL-1160, October 1972.
4. K. Leary, D. H. Templeton, A. Zalkin and N. Bartlett, The Crystal Structure of $[\text{XeF}_5]_2\text{PdF}_6^{2-}$, LBL-1171, December 1972.
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B. SOLID STATE CHEMISTRY AND PHYSICS

Norman E. Phillips, Principal Investigator

1. HEAT CAPACITY OF SmS AT 0 AND 15 KBAR

Samuel D. Bader and Norman E. Phillips

An unusual class of materials that contains rare earth ions with nonintegral valence and "soft" magnetic moments has recently been recognized.¹ SmS exhibits the properties characteristic of the materials at pressures above 6.5 kbar, where it is metallic and the Sm ions appear to have a mixture of $4f^5$ and $4f^6$ configurations, but not at lower pressures, where it is an insulator with the $4f^6$ configuration. We have measured the heat capacity at 0 and at 15 kbar from 0.3 to 20°K. Susceptibility measurements¹ have shown that only the $4f^6$ configuration contributes to the susceptibility, and that the magnetic transition or divergence expected for the $4f^5$ configuration does not appear. The heat capacity measurements show a broad anomaly throughout the 0.3 to 20°K region that evidently extend to higher temperatures. It is clear that the entropy associated with the doublet crystal field ground state of the $4f^5$ configuration disappears over a very broad temperature range instead of by the usual magnetic ordering transition.

1. M. B. Maple and D. Wohlleben, Phys. Rev. Letters 27, 511 (1971).

2. HEAT CAPACITY OF PrCu₂

Gary P. Schwartz, M. Wun, and Norman E. Phillips

Earlier heat capacity measurements¹ on PrCu₂ showed an anomaly near 6°K and the high temperature side of an anomaly that peaked below 0.06°K. The 6°K anomaly was interpreted as a crystal field effect that left the Pr³⁺ ions in a singlet crystal field ground state, and the lower anomaly was interpreted as indicating cooperative nuclear ordering. We have remeasured the heat capacity and obtained results that are sufficiently different to suggest that the interpretation must be modified. The 6°K anomaly is higher and sharper than a Schottky anomaly, suggesting that transition involves cooperative effects. The 0.06°K anomaly is not as high as the earlier work showed, and it is therefore less obvious that the

associated transition is cooperative.

1. K. Andres, E. Bucher, J. P. Maita, and A. S. Cooper, Phys. Rev. Letters 28, 1652 (1972).

3. THE HEAT CAPACITY OF DILUTE Cu Mn ALLOYS

W. E. Fogle, Gary P. Schwartz, and Norman E. Phillips

The very low Kondo temperature of dilute Mn in Cu makes it possible to study the interactions between the Mn spins and of the Mn spins with the conduction electrons at temperatures at which the Kondo spin compensation does not occur. We have initiated a program of heat capacity measurements on samples with concentrations from 100 to 1000 at. ppm and at temperatures between 0.06 and 25°K. Preliminary analysis of the data suggests that the contribution to the heat capacity of isolated impurities is separable.

4. THE LOW-TEMPERATURE HEAT CAPACITY OF NEODYMIUM

Mary M. Conway, W. E. Fogle, and Norman E. Phillips

The heat capacity of β -cerium showed a large, weakly field-dependent, temperature-proportional term that dominated the heat capacity to temperatures of the order of 0.1°K, below which it was masked by the hyperfine heat capacity of impurities. To see whether similar heat capacities might be found in other rare earth metals, we have measured the heat capacity of a neodymium sample enriched to 99.8% in even-even isotopes. In zero field the heat capacity of neodymium is similar to that of cerium, but the field dependence is much stronger. The measurements made so far suggest that the linear term in the high-field limit is of the order of magnitude of that usually expected for the electronic heat capacity. Tentatively, we conclude that the large zero-field linear terms in both neodymium and cerium are probably of magnetic origin even though the field dependence is very weak in cerium.

5. RESEARCH PLANS FOR CALENDAR YEAR 1973

Norman E. Phillips

Calorimetric investigations will be made on:

(1) Dilute Magnetic Alloys. In addition to the systems currently under investigation, Cu Mn and Au Gd, we plan to make measurements on $(La_{1-x}Gd_x)Al_2$, which is a superconductor containing localized moments, and possibly on additional rare earth solutes in noble metals. There is now experimental evidence that the Kapitza resistance between 4He and a metal can be reduced by the introduction of Gd impurities and the suitability of other rare earths might be predictable from heat capacity measurements.

(2) Other rare earth compounds that appear to show mixed configurations on rare earth ions, e.g., Yb Al₂

(3) Zeolites. There has been a renewed interest in the heat capacities of amorphous dielectrics. Zeolites have some of the features of amorphous substances, voids, but not others, disorder, and may provide some insight into the anomalous heat capacity.

(4) Liquid 4He . Rebuilding the apparatus for measurements to lower temperature will be continued.

(5) Work on apparatus for temperature scale measurements and possibly other experiments in the mK region will be continued.

6. 1972 PUBLICATIONS AND REPORTS

Norman E. Phillips and Associates

Journals

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3. T. E. Katila, N. E. Phillips, M. C. Veuro, and B. B. Triplett, Heat Capacity of, $Tm_2(SO_4)_3 \cdot 8H_2O$ Between 0.08 and 20 K, Phys. Rev. B 6, 1827 (1972) (LBL-858).

LBL reports

1. M. M. Conway, The Low-Temperature Heat Capacity of Cerium Metal (Ph.D. thesis), LBL-827, May 1972.
2. M. P. Mathur, M. Ashkin, J. K. Hulm, C. K. Jones, M. M. Conway, N. E. Phillips, H. E. Simon, and B. B. Triplett, Specific Heat of SnTe Between 0.06K and 30K Under Strong Magnetic Field, LBL-1137, August 1972; To be published in the Proc. of the 13th Intern. Conf. on Low Temp. Phys. Boulder, Col., August 1972.
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6. D. B. McWhan, J. P. Remeika, S. D. Bader, B. B. Triplett, and N. E. Phillips, Heat Capacity of Metallic V_2O_5 at High Pressure, submitted to Phys. Rev. (LBL-1467, Sept. 1972).

George Jura, Principal Investigator

1. HEAT CAPACITIES AT HIGH PRESSURES

A number of years ago, our group undertook the development of a method for the determination of the specific heats of metals and alloys under pressure. No calorimetric method available at that time was applicable for the objective, the determination of the specific heat under pressure. The method used was the development of a pulse technique, but because of the very large heat leak, the work had to be done on the microsecond rather than the millisecond scale. Thus the entire effort has been to develop pulse calorimetry on this time scale.

Originally, we wrote the following equation that related the heat capacity to the quantities that could be determined:

$$\frac{dE}{dt} = \frac{I^3 R_0 R'}{C_p} - k(T - T_a), \quad (1)$$

where E is the voltage across the sample when a constant current I is pulsed through the sample, R_0 the resistance of the sample at the initial temperature, $R' = dR/dT$, k the heat leak constant, T the temperature of the sample, and T_a the temperature of the ambient. In the limit of $T=0$, this reduces to

$$\frac{dE}{dt} = \frac{I^3 R_0 R'}{C_p} \quad t=0 \quad (2)$$

The experiments then consisted of sending constant current pulses through the sample, detecting the voltage drop on an oscilloscope, and then determining the best value of dE/dt as t approached 0.

There were difficulties with this technique, namely, the determination of 0 time. First, there is a rise time of the order of about 50 μ sec for the pulse, and then there is additional ringing, leaving about the first 100 μ sec that is not representative of the situation that was desired.

However, encouragement was given to the method in that when iron was investigated from about 100-298°K, and from pressures ranging from 25-100 kbars, reasonable results were obtained. It was known that the technique did not work for a metal such as aluminum.

Thus, this year, the treatment of the data

was studied, and the experimental conditions changed so that the method could be completely generalized. In order to do this, it was necessary to remove all restrictions on the equation used for the determination of the heat capacity. This last enables us to determine the heat leak constant as well as the heat capacity, and to approximate the change in the ambient temperature with the passage of time. The results have been phenomenally good. Actually, the only place where the original assumptions work really satisfactorily is at one atmosphere. Indeed, it may well be that the greatest use of the presently developed technique will be its application to high temperatures at one atmosphere.

What we have found is that if the resistance of the sample is sufficiently high, then for a period of about 500 μ sec the ambient can be considered as constant. For low-resistance material such as aluminum it is necessary to consider the change in the ambient.

If the ambient is considered as constant, and it so appears for high-resistance material, the integration of Eq. (1) gives

$$E - E_R = C(t - t_R) + tD(t - t_R)^2 + \dots,$$

where E is the voltage at time t, E_R the voltage at time t_R , $C = AER + B$, $D = A(AER + B)/2$. In these constants, $A = I^2 R' - k/C_p$ and $B = kE_0/C_p$. In the expression E_0 is the voltage at zero time. If the reference voltage is taken at the center of the available interval and if the time intervals are equally spaced, very little error is introduced in the solution for C and D. In principle, k and C_p could be determined from their respective values when different values of the current are used in the pulse. However, this leads to an uncertainty of about 20% in the values for the two desired quantities, since two equations must be solved. It is much better to approximate E_0 , which can be done to about 0.2%, and doing this we have found that C_p and k can be determined to an uncertainty of about 0.3 and 1% respectively. This has been done for iron and bismuth.

In the event that the variation in the ambient must be considered, we have found it satisfactory to write the original differential equation of the form

$$\frac{dE}{dt} = \frac{I^2 R_0 - k}{C_p} + \frac{b}{C_p} (E_0 + \alpha t),$$

where we have assumed that for the time under investigation the ambient is a linear function of time, and α is the proportionality constant. Unquestionably this is too simple, but since this correction is on the order of 10% at small times, a large error in it has relatively small effect on the final result. This treatment has been applied to aluminum, and the results are satisfactory.

A word about the instrumentation. The pulse generator that we have built is satisfactory. However, the detector we are using, an oscilloscope, is not the best. First, the values of the voltage obtained from reading the photograph are in error by an amount that is larger than desired. Secondly, the time required to measure the photographs to the desired accuracy is about 5 hours. Time of reading, and more accurate results could be obtained with better instrumentation. For example, the use of a 12-bit transient detector would give the value of E to 0.1% rather than the 1% we are now getting. The appropriate instrumentation to take the data from the recorder could and would save well over 5 hours. There are other techniques besides the one mentioned that would accomplish the same purpose. The problem is money. Any method other than that which we are using would cost a minimum of \$5,000, and the most ideal about \$10,000. We are going to attempt to obtain a grant for this equipment.

2. HEAT CAPACITY IN IRON AND ALUMINUM

George Jura and Tang-hua Chen

Some of the data obtained by Yee in earlier work on iron were remeasured and recomputed using the constant ambient temperature approximation. The relative values of the heat capacities were the same as reported by Yee,¹ though the absolute values were different.

Iron was done at one atmosphere from 298 to about 1000°K. The results are shown in Fig. 1. The solid line is from data in the literature, while the circles are the points obtained in the present investigation. It is only around 1000°K that the discrepancy is as high as 2 to 3%. Undoubtedly, this discrepancy is due to the inability to obtain good values for dR/dT in this region. Apart from this region, the variation between the previously observed results is only a few tenths percent. In the present technique the time scale was so short that it was not necessary to make any corrections for radiation loss. There is little question in our minds but that these data can be extended to very much higher tempera-

Fig. 1. Comparison of literature and present values for the heat capacity of iron from room temperature to about 1100°K. (XBL 731-2119)

Fig. 2. The heat capacity of aluminum at 298°K as a function of pressure.

(XBL 731-2120)

tures than here reported.

It has also been possible to detect differences between partially and completely annealed iron in this kind of experiment. We believe that this is the fastest, and with proper instrumentation, the best available method for obtaining specific heats at high temperatures at one atmosphere.

The big success of the new technique, we believe, is in the determination of the heat capacity of aluminum. Figure 2 shows the present results at 298°K from 25-100 kbars. The results, within error, about 3%, indicate that the heat capacity is constant. Earlier work, from an approximation of the Debye temperature as a function of pressure, would predict a 1% decrease in the heat capacity in

this range. The graph also shows the best results of our earlier work.

1. A. F. Yee, Heat Capacity of Iron as a Function of Pressure and Temperature (Ph.D. thesis) LBL-180, Nov. 1971.

3. HEAT CAPACITY OF BISMUTH

George Jura and Berardo Jurado

One of us (BJ) has spent his time on bismuth. He has not as yet obtained dR/dT , and therefore it is essential to give only C_p/R' . For his studies, it is possible to assume the ambient to be constant. Table I is an example of the sort of results now being obtained.

Table I. Variation in the heat capacity and heat leak constant as a function of current at 64 kbars.

I	C_p/R'	k/R'
4.5	1.40	0.91
4.6	1.37	0.96
4.7	1.37	0.98
4.8	1.31	1.10
4.9	1.39	0.95
5.0	1.32	1.09
5.1	1.36	1.02
5.2	1.35	1.03
5.3	1.33	1.07

He has also performed experiments in AgCl and a mixture of TlBr and TlI mixtures as the surrounding medium. The heat conductivity of the thallous mixture is lower than that of the silver chloride, and therefore should behave better in these experiments than the more usual chloride. Insofar as can be told, to a pressure of 80 kbar, the relative values of the heat capacity are the same with either medium.

Not all of the data have been properly treated as yet. Table II gives some of the results. There is a known phase transition between 78 and 87 kbars. This accounts for the huge change that is listed.

Table II.

P	C_p/R'
34.8	3.54
50.1	2.90
65.4	2.72
78.5	2.25
87.8	1.48

Figure 1 is a compilation of several sets of data for the heat leak constant when AgCl is the surrounding medium. The constant rises to a maximum around 80 kbars, and then either falls or levels off. There is a known phase transition in AgCl at about this pressure. Hopefully, it may be possible to relate the heat conductivity of the surrounding medium to the heat leak constant. If this proves to be feasible, it will also be able to determine or approximate the heat conductivity as a function of pressure, which would make some geophysicists happy.

Fig. 1. The heat leak constant when silver chloride is used as the surrounding medium, as a function of pressure at 298°K.
(XBL 731-2121)

4. RESEARCH PLANS FOR CALENDAR YEAR 1973

George Jura

We will continue in the development of a method for determining the specific heats

of metals and alloys under high pressures. As discussed in paper 1 of this section. We hope to find the right instrumentation to record the data. We are attempting to obtain a grant for the right equipment.

5. 1972 PUBLICATIONS AND REPORTS

George Jura and Associates

Journal

1. C. K. Wu, G. Jura, and M. Shen, Grüneisen Parameters of Crystalline Polyethylene, J. Appl. Phys. 43, 4348 (1972).

Gabor A. Somorjai, Principal Investigator

1. LOW ENERGY ELECTRON DIFFRACTION STUDIES BY SURFACES

a. Low Energy Electron Diffraction and Work Function Studies of Benzene, Naphthalene, and Pyridine Adsorbed on Pt(111) and Pt(100) Single-Crystal Surfaces

John L. Gland and Gabor A. Somorjai

Benzene, naphthalene, and pyridine adsorb readily on the Pt(111) and Pt(100)-(5x1) surfaces. Adsorption of these aromatic molecules leads to the formation of ordered structures on the Pt(111) surface, while adsorption on the Pt(100) surface leads to the formation of poorly ordered surface layers. Benzene adsorbed on the Pt(111) surface at 25°C causes the formation of the

Pt(111)- $\begin{bmatrix} -2\hat{a} & 2\hat{b} \\ 4\hat{a} & 4\hat{b} \end{bmatrix}$ -Benzene structure (Fig. 1A) with a corresponding work function change of

Fig. 2. Work function change as a function of exposure time for benzene on the Pt(111) surface. The pressures should be multiplied by 5.7 to give the effective pressure at the surface. (XBL-7210-4204)

approximately -1.4 V. With further benzene exposure the initial ordered structure is transformed to the

Pt(111)- $\begin{bmatrix} -2\hat{a} & 2\hat{b} \\ 5\hat{a} & 5\hat{b} \end{bmatrix}$ -Benzene structure (Fig. 1B)

with a work function change of approximately -0.7 V. The work function change as a function of exposure is shown in Fig. 2. This transformation is the result of a reorientation of the adsorbed benzene molecules. Naphthalene forms the Pt(111)-(6x6) naphthalene structure when adsorbed on the Pt(111) surface at 150°C, and the work function change on adsorption is

Fig. 1A) A LEED pattern of the Pt(111)- $\begin{bmatrix} -2\hat{a} & 2\hat{b} \\ 4\hat{a} & 4\hat{b} \end{bmatrix}$ -Benzene structure at 29 V.
B) A LEED pattern of the Pt(111)- $\begin{bmatrix} -2\hat{a} & 2\hat{b} \\ 5\hat{a} & 5\hat{b} \end{bmatrix}$ -Benzene structure at 29 V. (XBB 7211-5893)

about -2.0 V. Pyridine forms two poorly ordered structures on the Pt(111) surface. The large work function change on adsorption of pyridine (-2.5 V) indicates that the nitrogen participates in the adsorbate-substrate bond.

b. Low Energy Electron Diffraction and Work Function Studies of Substituted Benzenes Adsorbed on Pt(111) and Pt(100) Crystal Surfaces

John L. Gland and Gabor A. Somorjai

Low energy electron diffraction and work function change ($\Delta\phi$) measurements have been made for a series of substituted aromatic compounds adsorbed on the Pt(111) and Pt(100)-(5x1) surfaces. Benzene, toluene, t-butylbenzene, styrene, benzonitrile, nitrobenzene, and aniline all adsorb on both Pt surfaces studied. On the Pt(111) surface, benzene forms two well-ordered structures,

the Pt(111)- $\begin{pmatrix} -2\hat{a} & 2\hat{b} \\ 4\hat{a} & 4\hat{b} \end{pmatrix}$ -Benzene structure

($\Delta\phi \sim -1.4$ V) and the

the Pt(111)- $\begin{pmatrix} -2\hat{a} & 2\hat{b} \\ 5\hat{a} & 5\hat{b} \end{pmatrix}$ -Benzene structure

($\Delta\phi \sim -0.7$ V).

The transition between structures is facilitated by increased exposure of the surface to benzene. The initial ordered structure is associated with a π -bonded surface species; the second with a singly dehydrogenated, σ -bonded surface species. For toluene and t-butyl benzene adsorbed on the Pt(111) surface, the surface layer is poorly ordered, with a spacing three times the underlying lattice vectors, and is fairly exposure-independent. Although reorientation appears to be a major effect for benzene on the Pt(111) surface this effect is much less important for toluene and t-butyl benzene on the Pt(111) surface as indicated by analysis of the work function change data. All the singly substituted aromatic compounds studied form similar poorly ordered adsorbed layers with a characteristic distance three times the underlying lattice vector on the Pt(111) surface at 25°C. Nitrobenzene forms the Pt(111)-(4x2)-Nitrobenzene structure at 100°C.

On the Pt(100) surface, benzene forms a poorly ordered adsorbed layer with a characteristic distance twice the substrate unit cell size. Toluene t-butyl benzene, nitrobenzene, and aniline form poorly ordered adsorbed layers on the Pt(100) surface with a characteristic distance three times the spacing in the underlying layer. Benzonitrile and styrene form disordered layers on the Pt(100) surface.

c. Low Energy Electron Diffraction Studies of Stepped Platinum Surfaces and Ordered Carbon Surface Structures

Kenneth Baron, Donald W. Blakely, and Gabor A. Somorjai

A series of stepped platinum crystals with (111) orientation terraces and (100) steps that differ only in the widths of the atomic terraces have been studied. Surfaces with terraces of less than 4 atoms wide undergo faceting that is catalyzed by the adsorption of hydrocarbons. Stepped surfaces with wider terraces are stable and form many-ordered carbonaceous surface structures upon the chemisorption of hydrocarbons. The surface structure that forms depends on the type of hydrocarbon that is adsorbed and on the platinum surface structure. Platinum surfaces with steps of (310) orientation exhibit a high density of kinks. This surface does not form ordered carbon structures and is not reactive in surface reactions. These studies are continued to explore the role of the platinum surface structures in nucleating the formation of ordered carbonaceous deposits that appear to be important intermediates in catalytic reactions.

d. Low Energy Electron Diffraction Studies of the Clean and Sulfur-Covered (100) and (110) Crystal Faces of Vanadium

Clifford A. Megerle and Gabor A. Somorjai

Both the clean and the sulfur-covered (100) and (110) faces of vanadium were studied by low energy electron diffraction (LEED) and Auger electron spectroscopy. A cleaning treatment, involving the heating of vanadium in oxygen, was devised to facilitate the preparation of a clean vanadium surface. The diffraction pattern obtained from the clean V(100) surface was streaked, indicative of one-dimensional disorder. LEED indicates that both the clean and the sulfur covered V(110) surfaces are ordered. The intensity of the various diffraction beams from the clean and sulfur covered V(110) surfaces were measured as a function of incident beam voltage. These experiments were carried out by the photographic method. In addition, the intensity of the (00) beam from the clean V(110) surface was measured as a function of sample temperature, at several incident beam voltages.

e. Measurements of the Diffraction Beam Intensities from the Clean Pt(100) and Pt(111) Surfaces and from Ordered Surface Structures of Chemisorbed Gases

John J. Wasiliczky and Gabor A. Somorjai

A photographic technique has been developed

to measure the intensities of low energy electron diffraction beams from crystal surfaces. The fluorescent screen is photographed as a function of electron energy by a pre-sensitized film and the uniformly developed negatives are analyzed by using a micro-densitometer. The integrated relative intensities of the various diffraction beams from the clean (111) and (100) platinum surfaces and from acetylene surface structures have been obtained this way. The intensities so obtained are compared with the calculated relative intensities obtained by computer calculations.

f. Determination of the Surface Geometry for the Aluminum (100), (111), and (110) Surfaces by Comparison of LEED Calculations with Experiment

Marlo R. Martin and Gabor A. Somorjai

Intensity-vs.-incident electron energy (I-vs.-eV) curves are obtained for the (00)-, (11)-, and (20)-beams diffracted from the (100) surface of aluminum. The beam intensities, calculated by using a t-matrix formalism, are sensitive to small variations in the input parameters (number of phase shifts and atomic layers, order of multiple scattering, Debye temperature, incident beam angle, inner potential models and position of the surface atoms). The use of low energy electron diffraction for surface structure determination depends on the sensitivity of the I-vs.-eV curves to small variations of the surface geometry. The reliability of this method depends on the lack of sensitivity of these calculated curves to variations of the non-geometrical input parameters consistent with our knowledge of the physical processes involved. We conclude that the two most sensitive input parameters are variations in the incident beam angle and small displacements of the surface layer perpendicular to the surface. The inclusion of three layers parallel to the surface and five phase shifts is sufficient to obtain reliable calculated I-vs.-eV curves for the (100) face of aluminum. The use of a Debye temperature for the surface layer which is smaller than that of the bulk layers is shown to attenuate the I-vs.-eV curves uniformly. Exclusive reliance on a peak position or on relative peak intensities appears to be unjustified due to unresolved uncertainties in the models for the ion-core potential and for the electron self-energy correction. Displacement of the surface layer parallel to the surface is shown to have the greatest effect on the shape of the non-(00)-beams intensity curves appearing in the direction of the displacement.

Low energy electron diffraction (LEED) calculations have been extended to the (110)

and (111) surfaces of aluminum in order to determine the spacing between the surface and bulk layers of the crystal. The Al (110) surface is found to be contracted by 10 to 15% from the bulk interlayer spacing, and the Al (111) surface is found to deviate from the bulk spacing by less than 5%. This amounts to a determination of the surface layer position to within 0.1 Å. Results of calculations on all experimentally measured beams for these surfaces are compared with the experimental results for several assumed interlayer spacings. These comparisons are made with respect to qualitative peak shapes, peak positions, and relative peak amplitudes of the specular and all measured non-specular beams from each surface. In order to achieve this agreement it has been necessary to include the four outermost crystal layers and to describe the ion-core potential with five phase shifts in the 40-150 eV energy range.

2. AUGER ELECTRON SPECTROSCOPY OF SURFACES

a. Auger Electron Spectroscopy Studies of Lead-Indium Alloys

Svent Berglund and Gabor A. Somorjai

The Auger spectra of lead-indium alloys with 4.53, 9.08, 28.63, 44.62, and 60.49 at.% lead and of pure Pb and In were monitored in the liquid and solid state. The relative intensities of Pb (92V) N₉₀ Auger peak and the In (403V) M₅N₄ s_N 5 peak were used to determine changes in surface composition. Determination of the temperature dependence of the Pb/In Auger peak intensity ratio has proved to be a sensitive detector of the change of surface composition with respect to the bulk composition. The surface layers of all of the alloy samples were richer in lead than in the bulk phase. Oxygen decreased while the presence of carbon increased the excess lead concentration at the surface. Both ambient gases or dissolved minute impurities that may segregate at the surface change the two-component system to a three-component system and may drastically alter the surface composition. Auger spectroscopy when coupled with suitable calibration of the peak intensities should be an excellent technique to study the surface thermodynamics of multi-component systems.

b. Auger Electron Spectroscopy Studies of Adsorbed Hydrocarbons on Platinum Crystal Surfaces

Jean Paul Deville and Gabor A. Somorjai

Auger spectroscopy studies of adsorbed

hydrocarbons on platinum surfaces have been initiated. The purpose of these investigations is to explore the possibility of distinguishing different types of molecules by their chemical shifts, by monitoring shifts in both the platinum and carbon Auger peak positions. Preliminary studies indicate that the NNV platinum Auger peak at 235V shifts by 3V to 238V in the presence of carbon deposit on the platinum surface while the KVV carbon Auger peak in graphite at 270V shifts to 271.6V for the carbon atom on the platinum surface.

3. CATALYSIS BY SINGLE-CRYSTAL SURFACES

a. Low Pressure Studies of Dehydrocyclization of n-Heptane on Platinum Crystal Surfaces Using Mass Spectrometry, Auger Electron Spectroscopy, and Low Energy Electron Diffraction.[†]

Kenneth Baron, Donald W. Blakely, Bernard Lang,[‡] and Gabor A. Somorjai

The dehydrocyclization of n-heptane on platinum crystal surfaces of area less than 1 cm² was studied in the temperature range of 100-400°C and at pressures in the 10⁻⁴ Torr range. The toluene formation rate was monitored in a static system by a mass spectrometer, the surface structure by low energy electron diffraction, and the surface composition by Auger electron spectroscopy. The (111) face and two types of stepped platinum crystal faces were used. The stepped surfaces exhibit a surface structure of ordered steps of monatomic height separated by terraces with (111) orientation for one face and by terraces of (100) orientation for the other. The initial rate of toluene formation on the stepped surface with (111) terraces is twice faster than on the surface with (100) terraces, and the reaction can be sustained in the presence of hydrogen for more than an hour. A new ($\sqrt{3} \times \sqrt{3}$)-R30° surface structure which develops in the course of the reaction or a (9 × 9) surface structure which appears upon heat treatment to 850°C has no detrimental effect on the reactivity. These surface structures can be attributed to the presence of ordered carbon at the platinum surface.

Under identical conditions, the toluene yield of the stepped surface with (100) terraces decreases steadily as a function of the number of doses and reaches the detection limit after about an hour. The low index (111) surface appears to be less reactive than the stepped surface with (111) terraces by at least an order of magnitude. Both of the less reactive surfaces become covered by a dis-

ordered carbon-containing layer during the reaction.

[†]LBL-499.

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b. The Hydrogenation and Dehydrogenation of Cyclohexane on Platinum Crystal Surfaces

Donald W. Blakely, Kenneth Baron, and Gabor A. Somorjai

The catalytic hydrogenation and dehydrogenation of cyclohexane has been monitored by mass spectrometer on various stepped platinum surfaces. The reaction path depends on the partial pressure of hydrogen. At low partial pressures the reaction product is benzene while at high H₂ pressures cyclohexane is formed. These studies are continuing to explore the structure sensitivity of the surface reaction.

c. Catalysis at High Pressure on Single-Crystal Platinum Surfaces

Daniel R. Kahn, E. E. Petersen, and G. A. Somorjai

An apparatus has been constructed to study catalysis on various faces of single-crystal platinum both in ultra-high vacuum (UHV) and at high pressure (1 atm). The UHV chamber consists of a 12-inch diameter stainless steel vessel with a 200 liter per sec ion pump and a titanium sublimation pump, and is capable of reaching an ultimate pressure of 5 × 10⁻¹⁰ Torr. The high pressure reactor is formed in the upper chamber by closing the knife-edge of a 3-inch i.d. stainless steel reactor cup onto a gold O-ring which has been previously seated onto the inside of the 6-inch reactor flange. The reactor cup is attached to the bellows drive mechanism and is capable of traversing the entire diameter of the reactor. The remaining five mini-flanges on the reactor flange are used to provide pressure, temperature, and concentration measurements inside the high-pressure reactor cup. A 1520 Varian Aerograph gas chromatograph equipped with dual thermal conductivity and flame ionization detectors is used to monitor the formation of products.

Experiments to date have concentrated on the feasibility of monitoring reaction products at high pressure (approx. 800 Torr) on a single stepped platinum crystal (Pt(s) - [7 (111) × (111)]) having a total surface area of 0.80 cm². Chemical reaction systems

under investigation are the hydrogenation of cyclopropane, the hydrogenation of propylene, the dehydrocyclization of n-heptane, and the isomerization and hydrogenolysis of neopentane.

Before each catalytic run, the crystal is heated in 1×10^{-6} Torr O_2 at 900-950°C for 120 minutes to remove carbonaceous surface residues. The crystal is then activated in a 1 atm H_2 environment prior to the introduction of a hydrogen/hydrocarbon reaction mixture. Results for the cyclopropane/ H_2 system reveal that without prior H_2 pretreatment, there is virtually no propane product formed, whereas the reaction does proceed at a rate very close to literature values when the crystal is pretreated in H_2 for 1 hr.

Work is in progress to determine the most suitable chromatographic operating conditions for each reaction system. Comparison of reaction rates for each system will then be made on various low index and stepped crystal faces of Pt.

4. MOLECULAR BEAM SCATTERING BY SURFACES

A. Scattering of Diatomic and Polyatomic Molecules from the (100) Crystal Face of Platinum

Lloyd A. West* and Gabor A. Somorjai

The angular distributions of thermal energy molecular beams of diatomic (CO , N_2 , O_2 , NO , H_2 , D_2) and polyatomic (CO_2 , N_2O , C_2H_2 , NO_2 , NH_3 , and methylene cyclobutane) molecules were monitored following scattering from the (100) crystal face of platinum. All of the gases studied (with the exception of ammonia) yielded directed scattering patterns with the maximum intensity peaked at or near the specular angle for scattering from a clean platinum surface or from a platinum surface covered by a layer of ordered graphite. Broad cosine-like angular distributions which were independent of incident angle were observed, however, for the cases of C_2H_2 scattered from an adsorbed layer of C_2H_2 and CO scattered from adsorbed CO . These results seem to indicate that efficient energy transfer between the surface atoms and gas molecules, as indicated by angular distributions, occur only in specific instances. Apparently, the incident particles are reflected whenever the non-localized vibrational energy modes of surface atoms and the translational energy of the incident molecules are of similar magnitude. The adsorption of gases may

lead to the formation of additional low frequency localized surface modes that can be excited by the incident molecules. The efficient transfer of energy via localized surface modes would increase the residence time of the incident molecules and could thus account for the cosine-like angular distributions observed for C_2H_2 and CO .

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b. Modification of Molecular Beam Apparatus

Wigbert J. Siekhaus and Gabor A. Somorjai

The existing molecular beam apparatus was modified to permit more detailed investigations of gas-surface reactions. The incident beam path length was shortened and the pumping speed in the scattering chamber increased to greatly enhance the apparatus signal-to-noise ratio, making possible the measurement of the scattered beam velocity. A variable-frequency chopper was installed in place of the original fixed-frequency chopper, permitting the study of surface reaction kinetics by the modulated beam technique.

c. H_2 - D_2 Exchange and Helium Scattering on the Stepped Platinum Crystal Surface

Steven L. Bernasek and Gabor A. Somorjai

A mixed beam of H_2 and D_2 was scattered from the clean Pt-S[$\bar{9}(111) \times (111)$] surface at 900°K and HD was detected in the scattered beam. The HD was present to the extent of 10% of the incident D_2 flux. In the mixed beam, prior to scattering from the surface, HD is present to the extent of about 1% of the incident D_2 flux, therefore the other 9% is HD actually formed at the surface. Previous studies of this reaction on the Pt(100) surface showed no detectable HD formation. Work is continuing to compare HD formation from this stepped surface and the Pt(111) surface and to elucidate the reaction mechanism for the H_2 - D_2 exchange.

The scattering distribution of a 300°K helium beam from the clean Pt-S[$\bar{9}(111) \times (111)$] surface was also studied. The scattering distribution was peaked at the specular angle and had intensity and angular width similar to helium scattering distributions from the Pt(100) crystal surface. The scattering intensity is much lower and the distribution broader, for the stepped surface of this study, than that of the helium scattering distribution from the Pt(111) crystal surface.

5. RESEARCH PLANS FOR CALENDAR YEAR 1973

Gabor A. Somorjai

Low energy electron diffraction studies of iron and molecular crystal surfaces (ice, naphthalene, etc.) will be initiated. Surface structure analysis and computer calculations will be carried out using vanadium and platinum single-crystal surfaces and surface structures of adsorbed gases.

Catalytic reaction studies on single-crystal surfaces at low pressures and at high pressures will be extended to include the cyclization of neopentane, hydrogenation of benzene, and dehydrogenation of cyclohexane.

Auger electron spectroscopy studies of hydrocarbons adsorbed on platinum surfaces will be carried out.

Molecular beam scattering studies of surface reaction of H_2 , D_2 , O_2 will be carried out by measuring the velocity of the scattered beam.

6. 1972 PUBLICATIONS AND REPORTS

Gabor A. Somorjai and Associates

Journals and books

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4. B. Lang, R. W. Joyner, and G. A. Somorjai, Low Energy Electron Diffraction Studies of High Index Crystal Surfaces of Platinum, Surface Sci. **30**, 440 (1972) (LBL-121).
5. B. Lang, R. W. Joyner, and G. A. Somorjai, Low Energy Electron Diffraction Studies of Chemisorbed Gases on Stepped Surfaces of Platinum, Surface Sci. **30**, 454 (1972) (LBL-175).
6. R. W. Joyner, B. Lang, and G. A. Somorjai, Low Pressure Studies of the Dehydrocyclization of n-heptane on Platinum Crystal Surfaces

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9. F. J. Szalkowski and G. A. Somorjai, Auger Electron Spectroscopy Investigations of the Surface Chemical Composition of Vanadium, the Vanadium Oxides, and Oxidized Vanadium: Chemical Shift and Peak Intensity Analysis, J. Chem. Phys. **56**, 6067 (1972) (LBL-444).
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12. G. A. Somorjai, R. W. Joyner and B. Lang, The Reactivity of Low Index [(111) and (100)] and Stepped Platinum Single Crystal Surfaces, Proc. R. Soc. Lond. A. **331**, 335-346 (1972). (LBL-863).
1. M. R. Martin and G. A. Somorjai, A Systematic Evaluation of the Sensitivity of Leed Calculations to Small Variations of the Input Parameters for the Aluminum (100) Surface, LBL-1114, August 1972.
2. Marlo Martin, A Computer Program to Calculate Low Energy Electron Diffraction Intensities, LBL-1418, December 1972.
3. Steven L. Bernasek and G. A. Somorjai, Nozzle Beams, A Source of Molecules with Intriguing Properties, LBL-1140, November 1972; submitted to J. Chem. Education.
4. J. L. Gland and G. A. Somorjai, Low Energy Electron Diffraction and Work Function Studies of Benzene, Naphthalene and Pyridine Adsorbed on Pt(111) and Pt(100) Single Crystal Surfaces, LBL-1422, December 1972; submitted to Surface Science.
5. G. A. Somorjai, Low Energy Electron Diffraction and Auger Electron Spectroscopy Studies of the Structure of Adsorbed Gases on Solid Surfaces, Conference on Surfaces, University of Missouri, Rolla, June 19-23, 1972; to be published in Surface Science, LBL-878, June 1972.

LBL reports

Lee F. Donaghey, Principal Investigator

1. GAS-SOLID PROCESSES

a. Chemical Transport Reaction Analysis for Crystal Growth of Binary and Ternary Chalcogenides*

Rajani B. Agnihotri and Lee F. Donaghey

The chemical transport reaction method of crystal growth in closed systems was analyzed for binary and ternary (AB_2X_4) chalcogenides ($X = S, Se, Te$). The Stefan-Maxwell equations for multicomponent diffusion were integrated to obtain concentration profiles of gaseous species along the transport path. Gas phase diffusion controlled kinetics were assumed to apply in the range of pressure between 10^{-5} and 3 atmospheres and for temperatures between 800 and 1500°K. A general solution for a set of simultaneous nonlinear equations was obtained by unconstrained minimization techniques. With chemical equilibrium assumed at solid-gas interfaces the simulation allows the prediction of the transport rate, the concentration profiles of gaseous species along the transport path, and the total pressure.

Studies of the chemical transport of CdS, ZnS, and MnS with iodine show that the transport flux typically increases with the thermal gradient and concentration of the transport agent. For transport of MnS with iodine, however, the product flux reaches a maximum with respect to the iodine feed

Fig. 1. MnS product flux chemically transported for fixed temperature gradients as a function of iodine feed concentration.

(XBL 7212-7344)

concentration for a given thermal gradient, because of the variation of equilibrium constants with temperature, as shown in Fig. 1.

The chemical transport of ternary chalcogenides with halogens as transport agents shows similar rate dependence on thermal gradient and transport agent concentration, but the increased number of gas phase species raises the complexity of the simulation problem.

* Abstracted from LBL-1404 (M.S. thesis).

b. Chemical Vapor Deposition of $GaAs_{1-x}P_x$, Reactor Design and Growth Kinetics*

Saleem A. Shaikh and Lee F. Donaghey

The chemical vapor deposition of $GaAs_{1-x}P_x$ from Ga(l), PH_3 , AsH_3 , HCl and H_2 source chemicals in a flow-through reactor was

Fig. 2. Schematic dependence of gas phase partial pressures in the gallium saturation, reaction, and deposition zones of the $GaAs_{1-x}P_x$ reactor.

(XBL 729-7010)

studied both theoretically and experimentally. Reactor designs and reactions were reviewed, phase equilibria were calculated from known reaction equilibria, and diffusion limited deposition kinetics were formulated. Thermodynamics of phase equilibria in the Ga-As-P-Cl-H system were studied for each of three zones of an experimental reactor, and deposition kinetics calculated based on a boundary layer model.

A schematic of the gas phase species concentration in the gallium saturation, reaction, and deposition zones of the reactor is shown in Fig. 2. The mole fraction x of GaP in the deposited solid solution and the deposition rate were computed as a function of input concentrations and temperature profile, and studied experimentally. The mole fraction of GaP in the solid solution was found to increase with substrate temperature with a rate dependent on several factors. The deposition rate, however, decreases with increasing substrate temperature and is relatively independent of input molar ratios. A critical HCl input was found for maximum utilization of the group V elements in the reaction in each of the diffusion controlled and surface reaction controlled regimes. The experimentally obtained alloy compositions of $\text{GaAs}_{1-x}\text{P}_x$ deposited on [100] Ge and [100] Si substrates agree well with predicted values, but the experimental growth rates were far below the expected rates.

* Abstracted from LBL-1149 (M.S. thesis).

c. Chemical Vapor Deposition Rate Analysis of Group III-V Compounds

Ronald H. Bissinger and Lee F. Donaghey

Factors affecting the deposition rate of chemical vapor deposition reactions involving group III-V compounds are under study for gas phase diffusion and mixed diffusion-surface reaction kinetic control. The primary rate process neglected in previous studies has been the effect of gas phase reaction within the thermal boundary layer adjacent to the substrate. Under high thermal gradients the shift in reaction equilibria with temperature decreases the deposition rate. The present study improves on previous analyses by including the mixed polymers of the group V elements, AsP , As_2P_2 , As_3P , and AsP_3 . The equilibrium constants for reactions in which these species participate, estimated from statistical thermodynamics, should be applicable to gas phase equilibria for any III-V compound alloy. The deposition rate analysis must include the mixed polymers

of the group V elements whenever the group III element is in excess of the stoichiometric amount required.

d. Reactive Sputtering

Conrad Wright and Lee F. Donaghey

A sputtering system is currently being constructed with the capabilities of dc and rf sputtering. The sputtering system will be used to explore reactive sputter deposition of magnetic oxide compounds, electrically conducting electrode materials for application in liquid crystal display devices, and compound catalysts. Sputtering rates will be studied, in addition to the effects of changes in film stoichiometry with reactive gas pressure and target composition.

2. CRYSTALLIZATION PROCESSES

a. Forced Convection During Czochralski Crystal Growth

Pei Shiun Chen and Lee F. Donaghey

Forced convection under conditions of Czochralski crystal growth was studied in the isothermal limit. In this method of crystal growth the liquid phase hydrodynamics significantly affect inhomogeneities in dislocation densities and dopant concentration in the growing crystal. The forced convection process was simulated experimentally at low temperature by using a transparent crucible and simulation crystal with ethylene glycol solutions as the working fluid. The simulation revealed several vortices whose surfaces of separation could be displaced by varying the rotation speeds and direction of the simulation crystal and crucible. When both rotated in the same direction (co-rotation) one stagnation surface separates two non-intermixing regions preventing complete bulk liquid homogeneity. During counter rotation two stagnation surfaces separate three non-intermixing regions. Crystal rotation controls the convection above the new stagnation surface and the rate of mass transfer across stagnation surfaces. The study is currently being extended to the non-isothermal case and to experimental studies of Czochralski growth of intermetallic and ionic compounds.

b. Segregation of MnCl_2 in NaCl During Czochralski Crystal Growth

Nguyen Trien and Lee F. Donaghey

Nonhomogeneous segregation of MnCl_2 in NaCl during Czochralski crystal growth were studied by electron diffraction, Raman

spectroscopy and internal oxidation. Divalent cation solubility is limited in alkali halides but dependent on growth rate transients. Thus, variations in crystal growth rate will produce double layers consisting of enhanced incorporation of (Mn^{2+} , VNa^{+}) and reduced incorporation, relative to the average solid concentration of Mn^{2+} . The enhancement bands can be observed by precipitating $MnCl_2$ at temperatures below the growth temperature, and by internal oxidation. The internally oxidized precipitate layers were studied in Czocharalski-grown crystal sectioned along the axis of growth.

Dark field electron microscopy revealed precipitates in aged specimens of 1-10 μ size on numerous crystallographic planes. The $MnCl_2$ substitutional impurity was detected

by Raman scattering since the impurity removes inversion symmetry in the NaCl lattice, making first-order Raman scattering possible. Several scattering frequencies were recorded in the range from 115 to 265 cm^{-1} .

c. Electrodeposition of Sodium Tungsten Bronzes

Calvin T. Chew and Lee F. Donaghey

The single-crystal growth of sodium tungsten bronzes with the general formula Na_xWO_4 , $0.2 < x < 0.9$, has been studied by electrodeposition at varying rates from molten mixtures of sodium tungstate and tungsten trioxide. These electrically conducting compounds have been recently suggested¹ as electrodes in alkali fuel cells where high electrical conductivity and resistance to corrosion and dissolution are required. In this study a single cell with a spherical cathode electrode was employed in crystal growth at constant current or at constant overpotential.

Surface morphologies of crystal growth source areas were examined by scanning electron microscopy. A multiple screw dislocation growth source is shown in Fig. 1, for the compound $Na_{0.8}WO_4$. In general the density of layer edges increased with electrolysis current. Dendritic breakdown of layer edges occurred at high current, accompanying an incorporation of secondary phases in the growing crystal.

1. D. B. Sepa, A. Damjanovic, J. O'M. Bockris, *Electrochim. Acta* **12**, 746 (1967).

d. Orthoferfite and Garnet Synthesis and Crystal Growth

Conrad Wright and Lee F. Donaghey

Rare earth orthoferfites of $SmFeO_3$ and $TbFeO_3$ were produced by hot pressing the oxide powders at temperatures up to 1400°C and 7000 psi for 10^4 seconds. Examination of the specimens by electron microprobe analysis revealed nearly complete reaction of the primary oxides. In many samples, however, traces of unreacted R_2O_3 and Fe_2O_3 in the hot pressed materials were observed, indicating that higher temperatures and pressures are necessary for complete reaction. Similar results were obtained on hot-pressing the rare earth garnets $Sm_3Fe_5O_{12}$ and $Th_3Fe_5O_{12}$.

Successful synthesis of $SmFeO_3$ was realized by a zone refining technique following partial reduction of the compound. Since the electrical conductivity of the stoichiometric constituent phases was not high enough to permit electron beam zone refining, an inter-

Fig. 1. A multiple screw dislocation growth source in $Na_{0.8}WO_4$ produced by fused melt electrolysis. (XBB 731-86)

mediate arc melting process was introduced and found essential for this synthesis. The orthoferrite oxides were first arc-melted into a polycrystalline rod at low oxygen partial pressures which then, because of the increased electrical conductivity, could be zone refined with electron beam heating.

e. Liquid Phase Epitaxy of Magnetic Garnet Films

Conrad Wright and Lee F. Donaghey

Isothermal liquid phase epitaxy has been employed for the purpose of producing uniform thickness low-defect-density magnetic garnet films on non-magnetic substrates. This method is based on the observation that melts of appropriate flux to garnet compositions can be supercooled over a temperature range, thus permitting epitaxial growth of the garnet films at constant temperatures. Melt compositions were composed of stoichiometric quantities of the rare earth oxides and an excess of Fe_2O_3 dissolved in a 50:1 weight ratio of $\text{PbO}:\text{B}_2\text{O}_3$ flux. Melts have been studied with oxide to flux ratios ranging from 4 to 14 mol %. Figure 2 shows a simplified garnet ternary system showing the various oxide and flux ratios used in the liquid phase epitaxial studies. The liquidus temperature was determined by gadolinium-gallium garnet (GGG) substrate immersion probes at various temperatures for each melt composition studied.

Fig. 2. Simplified ternary phase diagram showing the region of liquidus composition for growth of the garnet phase $\text{Gd}_{2-2x}\text{Tb}_{2x}\text{Fe}_5\text{O}_{12}$ by liquid phase epitaxy. (XBL 751-2056)

f. Heat and Mass Transport During Liquid Phase Epitaxy

Pravin Mundkur

Equations for simultaneous heat and mass transport during solidification of epitaxial layers were formulated for multicomponent systems. Limiting forms are being studied for the near-isothermal case where the

initial liquid and substrate temperatures differ, and for the temperature-dependent case where the substrate-liquid system boundary temperature is programmed. Conditions for which heat transport can be included in mass transfer controlled solidification from solution are currently under study for several processes.

g. Ternary Laminar Eutectic Morphology

Lee F. Donaghey

The Cd-Sn-Pb ternary eutectic reaction is unique in exhibiting a cooperative ternary laminar structure in which the Cd- and Pb-rich phase lamellae are separated by the Sn phase. The solidification-dependent morphological properties of ternary laminar eutectics in general and for the Cd-Sn-Pb eutectic in particular have been studied toward predicting microstructural properties from liquid phase diffusivities and interfacial free energies. The Cd-Sn-Pb eutectic morphology predicted from minimizing the dynamic system free energy is consistent with that observed experimentally. Measurement of interlamellar spacings, λ , in eutectics solidified at varying velocities, v , give the relation,

$$\lambda^2 v = 21.2 \mu\text{m}^3/\text{sec}$$

a fundamental relation for this microstructure.

h. Electro-optical Properties of Nematic Liquid Crystal Mixtures

Timothy L. Montgomery and Lee F. Donaghey

The guest-host interaction phenomena observed in nematic liquid crystals containing pleochroic dyes is under investigation in a study of the electro-optical properties on nematic liquid crystal mixtures. In the course of this study, phase-composition relations are being established for a number of nematic liquid crystal mixtures. Effects of film thickness, electric field strength, incident light intensity and wavelength, and different pleochroic dyes on the electronic color-switching ability of specific liquid crystal mixtures will be observed. Application of these effects to the development of optical display devices will also be explored.

3. SOLID ELECTROLYTE STUDIES

a. Design Criteria for Solid Electrolyte Electrochemical Cells*

Richard W. Headrick and Lee F. Donaghey

Factors affecting the accuracy of galvanic cells involving solid electrolytes in thermochemical measurements were studied with regard to cell design and operation. Because coexistence electrodes are particularly well suited for determining free energies of formation of metal oxide compounds, the cells

and

exhibiting low and high entropies of reaction, respectively, were examined for critical parameters.

The galvanic cells studied were based on the closed cell concept involving sealed electrode compartments. Design improvements include (1) interior thermocouples for accurate measurement of the electrolyte interface temperature, (2) individual gas and vacuum manifolds on the isolated half-cell compartments, (3) elimination of stray emf in potential leads, and (4) tapered alumina to glass wax seals to facilitate rapid electrode replacement and resealing.

The improvements introduced in galvanic cell structure led to standard free energy change determinations for the following reactions:

The most significant error in cell voltage (emf) measurements was found to arise from secondary electrode reactions with water vapor. Proper outgassing of the half-cells was determined to be extremely important, as even a slight amount of retained moisture caused higher cell emfs. Secondary electrode reactions with retained water vapor are proposed as a mechanism whereby emf data

from earlier studies, particularly those using "open cell" techniques, on the above systems is higher than that measured in this study. Incorrect temperature measurement due to thermal gradients around the electrolyte was also shown to be a source of error.

* Abstracted from LBL-839 (M.S. thesis), July 1972.

b. Activity Measurements in Liquid Metal Alloys Using Solid Oxide Electrolyte Techniques

Ray Pong and Lee F. Donaghey

The thermodynamic properties of liquid metal alloys are under study by solid oxide electrolyte galvanic cell techniques. Activities of group III elements in liquid alloys have been studied with both $\text{Zr}_{0.85}\text{Ca}_{0.15}\text{O}_{1.85}$ (CSZ) and $\text{Th}_{0.85}\text{Y}_{0.15}\text{O}_{1.925}$ (YDT) solid electrolytes in the low oxidation potential region where non-equilibrium processes occur. Instrumentation for the continuous monitoring of cell potential was constructed and its limitation explored. Component activity measurements in the In-Ga system utilizing the cell $\text{Pt}|\text{W}| \text{In:Ga} = \text{Ga}_2\text{O}_3 || \text{YDT, or CSZ} || \text{Ga:Ga}_2\text{O}_3|\text{W}|\text{Pt}$ show a time-temperature dependent decline in cell emf consistent with the finite electronic conductivity of the electrolytes. Properties of electrode reactions and of electrolytes are being studied to correct for non-equilibrium processes affecting activity measurements in liquid metals at low oxygen partial pressures.

The conditions under which solid oxide electrolyte techniques can be applied to thermodynamic property measurements of III-V compound alloys have been defined for each of several solid electrolytes. The range of allowable temperature and oxidation potential was determined for CSZ and YDT solid electrolytes by utilizing the most stable oxide and element as the reference electrode. The high vapor pressures of the group V elements imposes further restrictions requiring high pressure cells over some ranges of measurements.

c. Defect Structure of Gadolinium-Gallium Garnet

Conrad Wright and Lee F. Donaghey

The non-stoichiometric defect structure of gadolinium-gallium garnet (GGG) is being determined by electrical conductivity methods over a temperature range of 800-1500°C and from 1 to 10^{-15} atm of oxygen. The electrical

conductivity is measured by a standard dc four-point probe technique using Pt electrodes. The specimen is enclosed in an air-tight alumina cell with provisions for passing gas through the cell.

A gas-mixing manifold was designed to produce the desired oxygen partial pressures in the cell by appropriate dynamical mixing of CO and CO₂ gases. The manifold is capable of mixing the gases in a 1:100 to 100:1 ratio by the proper choice of orifices. Figure 1 shows the conductivity of GGG over a temperature range of 1000-1500°C for CO:CO₂ ratios of 47.4 and 0.85.

The conductivity method is currently being extended to magnetic thin films epitaxially deposited on GGG to determine defect structure of these films.

Fig. 1. Electrical conductivity of gadolinium-gallium garnet as a function of temperature and oxygen partial pressure.
(XBL 731-5645)

4. RESEARCH PLANS FOR CALENDAR YEAR 1973

Lee F. Donaghey

This program will continue to concern physicochemical methods involved in the

preparation and processing of solid state materials and the impact of processing on physical properties. Kinetics are emphasized in crystallization processes and in deposition from the gas phase. Epitaxial thin films of compound semiconductor alloys and magnetic oxide compounds will be studied through phase equilibria, defect structure, and processing effects.

Gas-phase etching kinetics of GaAs-GaP alloys will be studied. Group V polymer formation will be examined and related to the chemical vapor deposition process. X-ray topography will be employed to study the dislocation structure in graded-composition epitaxial layers.

Magnetic oxide compounds are under study by several techniques. An rf sputtering module is nearly completed, and will be used to reactively sputter orthoferrite and garnet compounds. Alternative solvents to PbO will be examined for preparation of garnet compounds by liquid phase epitaxy, and the deposition rate studied for simultaneous heat and mass transport. Magnetic properties and defect structure of garnet films applicable in magnetic bubble domain devices will be studied.

Phase equilibria in ternary liquid alloys of indium and gallium will be studied by solid electrolyte electrochemical cell techniques. Activity measurements are lacking for many group III-Va-Vb and group IIIa-IIIb-V compounds, yet can be measured directly by solid electrolyte galvanic cells.

Dopant segregation during Czochralski crystal growth will be studied in CaF₂. Metal-intermetallic eutectics will be grown by this method to explore thermal instabilities, thermal profiles and the effect of forced convection.

Electrodeposition studies of alkali tungsten bronzes will be directed toward measuring potential distributions and toward deducing the melt complexes taking part in crystal growth.

Phase equilibrium measurements of nematic liquid crystals containing pleochroic dyes by differential scanning calorimetry and optical scattering will continue toward determining temperature ranges over which electronic color switching and dynamic scattering can be obtained. Application of these effects to optical display devices will continue to be explored.

5. 1972 PUBLICATIONS AND REPORTS

Lee F. Donaghey and Associates

Journals

1. S. Bjorklund, L. F. Donaghey and M. Hillert, The Effects of Alloying Elements on the Rate of Ostwald Ripening of Cementite in Steel, *Acta Met.* 20, 867-874 (1972).*

Papers presented

1. L. F. Donaghey, Selected Topics in the Thermodynamics and Kinetics of Alloys with Reference to Steel, OAS Lectureship, Institute of Physics, National University of Mexico, Mexico City, June 12-30, 1972.
2. L. F. Donaghey, Direct Observation of Phase Transformations with High Voltage Electron Microscopy, *ibid.*, June 20, 1972.
3. L. F. Donaghey, Applications of Solid Electrolyte Galvanic Cells in Inorganic Materials Research, *ibid.*, June 27, 1972.
4. L. F. Donaghey, Materials Research at Berkeley, Institute for Advanced Studies, Polytechnical Institute, Mexico City, June 30, 1972.

5. L. F. Donaghey, Applications of Gas-Solid Reactions to Materials Coating, Chemical Engineering Colloquium, University of California, Berkeley, Dec. 6, 1972.

LBL reports

1. R. W. Headrick, Design Criteria for Solid Electrolyte Electrochemical Cells (M.S. thesis), LBL-839, July 1972.
2. S. A. Shaikh, Chemical Vapor Deposition of $\text{GaAs}_{1-x}\text{P}_x$, Reactor Design and Growth Kinetics (M.S. thesis), LBL-1149, September 1972.
3. R. A. Agnihotri, Chemical Transport Reaction Analysis for Crystal Growth of Binary and Ternary Chalcogenides, (M.S. thesis) LBL-1404, December 1972.
4. P. S. Chen and L. F. Donaghey, An Experimental Study of Forced Convection during Czochralski Crystal Growth LBL-1432, December 1972.
5. R. W. Headrick and L. F. Donaghey, Design Criteria for Solid Electrolyte Electrochemical Cells, LBL-839 Rev., December 1972.

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C. ELECTROCHEMISTRY

Charles W. Tobias, Principal Investigator

1. FUNDAMENTAL STUDIES OF IONIC MASS TRANSPORT

a. Distribution of Ionic Mass Transport Rates in a Flow Channel

Uziel Landau and Charles W. Tobias

Studies of the local maximum mass transport rates along planar electrodes in channel flow were extended to the turbulent regime. Local transport rates were measured by using the limiting current technique for copper deposition from acidified copper sulfate solutions on a segmented copper electrode embedded in the wall of a flow channel. The pilot plant scale flow circuit and its instrumentation were reported earlier.¹

Pressure-distribution measurements taken in the flow channel in the turbulent flow regime prove that a fully developed hydrodynamic turbulent flow profile has been established. Well-defined limiting current plateaus were obtained up to Reynolds number of 100,000 (corresponds to linear velocity of 300 cm/sec.). The power dependence of Nusselt number on the Reynolds and Schmidt numbers obtained experimentally is in agreement with existing correlations for mass transport in turbulent flow.

Special attention was paid to the entrance region where mass transfer rates are higher.

Fig. 1. Experimental mass transfer rates in the entrance region. (XBL 731-2144)

Accuracy in this region was obtained by using narrow cathode segments which enabled measurements of local mass transfer rates. Figure 1 shows the ratio of Nu/Nu_0 as a function of distance along the plate expressed in equivalent hydraulic diameters. As expected, the mass transfer entrance region narrows down with increasing flow rates; here the local Nusselt number is proportional to the inverse cube root of the distance from the leading edge.

1. Uziel Landau and C. W. Tobias, Flow Circuit for Ionic Mass Transfer Studies at High Flow Rates, IMRD Annual Report for 1970, UCRL-20500, April 1971, p. 39.

b. Mechanism of Electropolishing of Copper^{*}

Kaoru Kojima and Charles W. Tobias

Diffusion kinetics of the active dissolution of copper in phosphoric acid was studied under both galvanostatic and potentiostatic conditions. In agreement with Elmore, and Hickling et al., the first voltage rise in galvanostatic experiments, as well as the onset of current decrease in potentiostatic experiments, is interpreted to be caused by exceeding the solubility limit of copper phosphate at the anode surface. The potential or current value respectively can be predicted by evaluating the rate of transport of copper phosphate away from the surface.

Re-examination of published experimental data, as well as numerical evaluation of a newly proposed theoretical model, indicates that in electropolishing the concentration of phosphoric acid at the anode surface is far from zero: $pH \approx 2$.

Correction of literature values of anodic overpotential for ohmic potential drop between anode and reference electrode and for concentration overpotential reveals that in the active dissolution range the behavior of charge transfer overpotential can be well represented by the Tafel relation; the calculated value of α_a is similar to that reported for dissolution of copper in acid sulfate media.

The characteristic current peak separating the active dissolution region from the current plateau, where polishing occurs, is shown to result from increasing coverage of the anode surface by cuprous oxide with increasing applied potential.

Thermodynamic and transport calculations lead to a coherent picture of the stability of cuprous and cupric oxides in the brightening-polishing range. A reinterpretation of impedance data obtained by Chashi et al. on oxide-covered copper anodes indicates that the range of thickness of the invisible layer responsible for the polishing action is 13 - 124 Å. Optical observations, thermodynamic calculations, and impedance data indicate that in the polishing region the oxide covering the surface is multilayered, probably composed of layers of Cu_2O , CuO , and a higher oxide of copper.

A method is presented for the prediction of the current density range suitable for electropolishing under various hydrodynamic conditions.

* Abstract of LBL-140, February 1972.

2. ELECTROLYSIS AT HIGH CURRENT DENSITIES

a. Mass Transfer at Closely Spaced Planar Electrodes

Raul E. Acosta, Rolf H. Muller, and Charles W. Tobias

The program to establish working correlations for mass transfer processes under the conditions found in high current density electrolysis has been continued. These conditions, involving the use of a very small interelectrode gap (of the order of a few hundredths of a centimeter) and high flow rates, give rise to prohibitively large pumping requirements. However, for the same mass transfer rate (same mass transfer boundary layer thickness δ_M) the power requirement decreases with decreasing interelectrode gap (Fig. 1), making the use of small gaps less unattractive for large scale processes.

By using integral pressure transducers, the pressure drop along the channel cell described earlier¹ was determined in the range $1,000 < \text{Re} < 20,000$, to obtain the friction factor. These pressure measurements confirmed that the entrance length allowed ($80 D_h$) was sufficient to insure a developed velocity profile at the electrodes. Even though the cell walls had been polished to optical smoothness (the roughness measured with a profilometer² was of the order of 0.5 μ), the roughness factor for this cell is high (0.0005), since the interelectrode spacing is only 0.05 cm. This points out one of the uncertainties involved in using correlations

Fig. 1. Power required for pumping electrolyte between parallel planar electrodes. Based on: $\rho = 1 \text{ g cm}^{-3}$, $\gamma = 1 \times 10^{-2} \text{ cm}^2 \text{ sec}^{-1}$, $D = 4 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$. (XBL 728-3731)

for mass transfer data that appear in the literature: the data are often reported in terms of a fraction factor for "smooth" electrodes, even though this friction factor was not determined for the particular equipment where the mass transfer data were obtained.

Limiting current measurements have also been performed in the range $1,000 < \text{Re} < 20,000$ using three different channel widths (1, 1.5, and 2 cm) and an interelectrode gap of 0.05 cm (Fig. 2). The results confirm that for an aspect ratio (width/gap) greater than 20 the system may be considered to be formed by two parallel plates of infinite width.

A new cell and pneumatic pump have been installed and tested. This new system will allow the study of mass transfer rates using an interelectrode gap of 0.02 cm, in the same Reynolds number range. Roughness effects will be studied for both 0.05 and 0.02 interelectrode spacings, using a random sandblast finish and a geometric V groove pattern perpendicular to the flow direction.

Fig. 2. Mass transport to a planar electrode. Interelectrode gap = 0.05 cm. Electrolyte properties same as used in Fig. 1. (XBL 728-3761)

* Surfanalyzer 150 System, Clevite Corporation, El Monte, Calif.

1. Raul E. Acosta, Rolf H. Muller, and Charles W. Tobias, *Electrolysis at High Current Density: Mass Transfer Considerations*, IMRD Annual Report 1971, LBL-425, April 1972, p. 35.

b. Periodic Phenomena in the Anodic Dissolution of Copper

John F. Cooper, Rolf H. Muller, and Charles W. Tobias

Oscillations in anode potential have been observed during galvanostatic dissolution with a variety of metal/electrolyte combinations.^{1,2} Of particular interest are the regular saw-tooth potential oscillations which occur during the high current density dissolution of copper³ and low carbon steel⁴ in sodium chlorate solutions. Anode potential oscillations have been related to the periodic growth and rupture of anodic oxide films⁵ and may be

responsible for the favorable properties displayed by the sodium chlorate electrolyte in electrochemical machining applications.⁵

Galvanostatic dissolution of copper in sodium chlorate electrolytes occurs by ionic conduction of cuprous ions through a thin uniform oxidic film which forms on the surface of the metal. This film gives rise to a uniform surface impedance which results in a generally polished surface texture.

The upward sweep in potential is believed to be caused by the restriction of current on the anode film by the precipitation of a secondary layer of cuprous oxide and basic copper salts. At a given current density, the rate of accumulation of the secondary layer is controlled by the local concentration of hydroxyl and chloride ions and by the rate of convection of cuprous ion away from the surface.

The periodic rapid decreases in anode potential may be the result of a dielectric breakdown of the uniform oxidic film followed by a short period of active dissolution of the substrate. The abrupt fall in potential is accompanied by a spark discharge at the anode surface, followed by a rapid etching of the metal surface.

It has been found that similar oscillations may be produced in a variety of electrolytes (e.g., molar sodium nitrate, -sulfate, and -hydroxide) by the addition of small amounts of halide ions. Experiments are under way to relate the oscillations to the widely reported phenomenon⁶ of halide ion attack on anodic oxide films.

1. K. J. Vetter, *Electrochemical Kinetics* (Academic Press, New York, 1967), p. 786.
2. R. S. Cooper and J. H. Bartlett, *J. Electrochem. Soc.* 105, 109 (1958).
3. J. Cooper, R. H. Muller, and C. W. Tobias, "Periodic Phenomena in Copper Dissolution at Constant Current," paper presented at 138th meeting of the Electrochemical Society, October 4-9, 1970.
4. D. Jacquot, *ECM Studies of Engineering Materials in a Flow Channel Cell*, to be submitted for publication.
5. M. A. LaRoda and M. C. McMillan, *Electrochem. Tech.* 5, 340 (1967).
6. B. N. Kabanov, *Electrochemistry of Metals and Adsorption* (Freund Publishing House, Holon, Israel, 1969) p. 155.

3. ELECTROCHEMISTRY IN NONAQUEOUS SOLVENTS

a. Electrochemical Behavior of the Alkali Metals in Propylene Carbonate*

Jacob Jorň and Charles W. Tobias

The electroreduction of active metals from aqueous solution is restricted primarily by thermodynamic limitations, because of preferential decomposition of the solvent. The most reactive of these, the alkali metals, cannot be deposited at all from aqueous solutions. Propylene carbonate (PC), a highly polar aprotic compound, was used as solvent medium for the deposition of the alkali metals at ambient temperature. Li, Na, K, Rb, and Cs were deposited successfully from their chlorides in $AlCl_3$ solution in PC. $AlCl_3$ served as a complexing agent. The experimental program included:

1. Equilibrium potential measurements which yielded activity coefficient data, and served to establish a relative standard potential scale in $AlCl_3$ -PC.
2. Conductance and density measurements.
3. Micropolarization measurements, for obtaining kinetic information (exchange current densities, transfer coefficients) on the alkali metals and their amalgams in $AlCl_3$ -PC.
4. Electrodeposition studies in the Tafel region.

A new process is proposed for the production and separation of the alkali metals at ambient temperature. Alkali amalgam from commercial mercury-chlorine cells is transferred into an $AlCl_3$ -PC electro-refining cell, where the alkali metal is dissolved anodically from the amalgam, and deposited in a pure metallic form at the cathode. The lean amalgam is returned to the chlorine cell where it is again enriched with respect to the alkali metal.

* Abstract of LBL-1111, September 1972.

b. Reduction of Earth-Alkali Metals in Propylene Carbonate

Leonard Silvester and Charles W. Tobias

Exploratory work has been initiated on the electroreduction of calcium at ambient temperature by using propylene carbonate and related aprotic solvents.

The long-term stability of the $AlCl_3$ -PC system as used for electroreduction, separation, and electrorefining of Group I and II metals is being investigated.

4. RESEARCH PLANS FOR CALENDAR YEAR 1973

Charles W. Tobias

a. Fundamental Studies of Ionic Mass Transport

This program is designed to develop understanding of the effects of hydrodynamic flow on electrode processes in models, which have clear-cut significance in applied electro-synthesis, batteries, and fuel cells. Emphasis will continue to be on flow between parallel planar electrodes. Integral limiting currents and distribution of limiting rates are measured in a systematic manner so as to enable us to propose correlations of general validity over broad ranges of Reynolds and Schmidt numbers. In addition, investigations will be extended to observe effects of flow on surface morphology during the electrodeposition of metals. A parallel effort will be conducted pertaining to the direct measurement of concentration gradients in the solution boundary layer by Mach-Zehnder interferometry (see project under R. F. Muller). Effective ways for the reduction of the boundary layer thickness by means other than bulk flow will be sought. These may include slurry flow and triggering entrance effects by periodic local interference with the boundary layer.

b. Electrolysis at High Current Densities

Transport phenomena in very high rate electrolysis (up to 100 A/cm²) will be quantitatively described to provide usable guidelines for the design and conduct of technologically significant processes (e.g., electromachining and electroforming). An understanding of the role of anodic oxide layers, particularly with reference to periodic fluctuations of anode potential, will be sought, so as to allow rational selection of electrolytes in electromachining. Development of new techniques for the electromachining of high strength materials will receive increased attention.

c. Electrochemistry in Nonaqueous Solvents

The feasibility of development of technologically significant processes for the recovery of reactive metals from their common salts and for their separation and purification using propylene carbonate as an ionizing solvent medium will be further explored. Work will continue in three areas:

- 1) preparation of alkali metal alloys (such as NaK) directly from halides,
- 2) separation of a single alkali metal from mixtures of alkali metals,
- 3) recovery of earth alkali metals.

Depending on funding levels, and on availability of qualified personnel, work on the separation and recovery of rare earth will also be undertaken.

5. 1972 PUBLICATIONS AND REPORTS

Charles W. Tobias and Associates

Journals

1. K. W. Beach, R. H. Muller and C. W. Tobias, A One-Dimensional Focusing Critical Angle Refractometer for Mass Transfer Studies, Rev. Sci. Instr. 43, 925 (1972).
2. L. F. Silvester, J. J. Kim, and P. A. Rock, Thermodynamics of Hydrogen-Isotope-Exchange Reactions: I. Electrochemistry in Dimethylformamide, J. Chem. Phys. 56, 1863-1869 (1972).

LBL reports

1. Koaru Kojima, A Study of the Mechanism of Electropolishing of Copper (Ph.D. thesis), LBL-140, February 1972.

2. Jacob Jornc, Electrochemical Behavior of the Alkali Metals in Propylene Carbonate (Ph.D. thesis), LBL-1111, September 1972.

3. K. W. Beach, R. H. Muller, and C. W. Tobias, Light Deflection Effects in the Interferometry of One-Dimensional Refractive Index Fields, LBL-1102, September 1972.

4. Koaru Kojima and Charles W. Tobias, Solution-Side Transport Processes in the Electropolishing of Copper in Phosphoric Acid, LBL-1106, July 1972.

5. Koaru Kojima and Charles W. Tobias, Interpretation of the Impedance Properties of the Anode-Surface Film in the Electropolishing of Phosphoric Acid, LBL-1129, August 1972.

Papers presented

1. Charles W. Tobias, Some Fundamental Aspects of Industrial Electrochemical Processes, keynote address, 23 rd meeting of the International Society of Electrochemistry, Stockholm, Sweden, August 27-September 2, 1972.

2. Charles W. Tobias, New Directions in Electrochemical Engineering, Acheson Medal Address, 142 nd meeting of the Electrochemical Society, Miami Beach, Florida, October 8-13, 1972.

Rolf H. Muller, Principal Investigator

1. OPTICAL STUDIES OF INTERFACIAL PHENOMENA

a. Interferometry of Mass Transfer Boundary Layers

Frank R. McLarnon, Rolf H. Muller, and Charles W. Tobias

When interferometric measurements of mass transfer boundary layers are made, light deflection in the refractive index field gives rise to errors¹ in the resulting interferograms. In order to check the computed effect of these errors, we investigated the electrodeposition of Cu from a stagnant layer of 0.1 M CuSO₄ at 10.0 mA/cm². Preliminary results showed interference fringes of the predicted shape, but they were displaced vertically (normal to the electrode working surface) by 20-50 μm from the predicted fringes. Also, an extraneous fringe shift and diffraction fringes at the electrode/electrolyte interface have been observed.

Factors contributing to these undesirable phenomena have been found to be (a) small errors (less than 0.5 mm) in focusing, (b) small errors (less than 0.2") in the alignment of the electrode surface with respect to the incident light beam (specimen beam), (c) small deviations from flatness (less than 20μm) of the electrode surface.

The following corrective measures have been taken: (1) Eleven sets of scale lines have been etched on one of the glass sidewalls at regular intervals along the 1.00 meter electrode length to ensure reproducible focusing. (2) A new pair of electrodes, each with one side face (3.81 cm high) polished flat to within 0.02" and optically smooth, has been built and installed. Thus, the incident light beam can be aligned within 0.02° by reflection from the side faces. (An uncertainty of 0.1° in the test beam angle may produce a 20 μm uncertainty in the apparent location of the 10 mm wide electrode surface.) (3) Each electrode working surface has been machined and polished to be at right angle to the polished side face used for alignment by reflection. A right-angle polishing jig of a new design has been used for this operation. Thus, the test beam can now be aligned parallel to the working electrode surface to approximately 0.05°. (4) New polishing techniques for the working surface of the electrode have been developed to reduce the rounding of the electrode edges.

Presently, the electrode center is about 10 μm higher than the edges.

We now find that the observed interference fringes agree with the predicted fringes to within a vertical displacement of 10 μm, even though some extraneous fringe shift and diffraction patterns are still present. New polishing abrasives are now being tested as a means of further reducing the rounding of the electrode surface. This effort is expected to reduce the uncertainty in the position of the electrode surface, the extraneous fringe shift and the diffraction patterns in the interferograms still further.

A function relating electrolyte concentration to a 4th order polynomial in vertical distance from the electrode surface has been found to successfully approximate the concentration profiles we have studied. This functional relationship will be used in the interpretation of concentration boundary layers resulting from convective transport.

Convective transport boundary layers in channel flow will now be investigated by interferometry and focusing refractometry and interpreted using light deflection considerations and polynomial curve fitting.

1. IMRD Annual Report, LBL-425 (1971), p. 39.

b. Automatic Ellipsometry

H. Jörg Mathieu and Rolf H. Muller

A self-compensating automatic ellipsometer with fast response and high resolution has been built for the measurement of thin films on metal surfaces.

The principal purpose of the construction was to reduce the time (several minutes) required for a manual measurement, so that transient films could be monitored continuously. A slewing rate of 1.8°/ms over a dynamic range of ±7° has been achieved for the azimuth readings of polarizer and analyzer. This rate compares to a value of 4°/s reported before for a partially functioning instrument, based on the same operating principles.¹ Under conditions which result in an azimuth change of a full turn for a film thickness increment of one wavelength, we therefore expect to be able to follow film growth at rates up to 2.5 μm/s.

Another purpose of the construction was

Fig. 1. Block diagram of self-nulling ellipsometer

- A Analyzer
- AF Analyzer Faraday cell
- C Collimator
- CT Controller
- DVM Digital voltmeters (2)
- F Filter ($\lambda = 546.1 \text{ m}\mu$)
- G Galvanometer light beam oscillograph (channels 1-6)
- L High pressure mercury arc lamp
- M Modulation amplifier (10 kHz)
- O Oscillator
- P Polarizer
- PF Polarizer Faraday cell
- PM Photo detector
- PS High Current Power Supply (dc)
- Q Compensator
- S Specimen
- T Telescope

(XBL 7212-4927)

to maintain an optimum resolution of the electronic azimuth readings in the fast mode of operation and to increase it over the best manually obtainable resolution of 0.01° in a slower mode. With a uniform, highly reflecting surface, a resolution of 0.01° has been demonstrated in the fast mode. This resolution decreases to 0.08° with a surface of poor optical quality. An increase in response time up to 5s (slow mode) has provided resolution down to 0.002° . Under the conditions specified above, this resolution in azimuth corresponds to a detection limit of approximately 0.01 monolayers of Kr and proportionally less for larger molecules.

The instrument employs an electronic rotation of the plane of polarization of incident and reflected light by means of two Faraday cells, to take the place of the

mechanical rotation of polarizer and analyzer prisms, over the dynamic range. A control signal is derived from a 10 kHz modulation of the Faraday rotation to drive a null-seeking control loop. Current measurements of the Faraday coils are used as azimuth readings and displayed in two digital voltmeters, calibrated in degrees of azimuth rotation with readings to 0.001° . The signals are also recorded by a multiple-channel light beam oscillograph. A schematic of the instrument is given in Fig. 1.

In situ observation of transient anodic films on metal surfaces in a newly-built cell with exchangeable electrodes has been initiated.

c. Computer Programs for Ellipsometry

H. Jörg Mathieu

A short program (PSIDEL) has been written to convert ellipsometer circle readings into relative phase Δ and amplitude parameter ψ . The program determines the zone of a measurement and provides two- or four-zone averages.

The correction of systematic errors of analyzer, polarizer, and compensator circle reading, together with the deviation of the compensator from ideal retardation and transmission, has been incorporated in the computation of optical constants of bare surfaces derived from measurements in one zone (program OZOM).

Several previously used programs for the interpretation of ellipsometer measurements have been modified. Two of them have been converted to Fortran IV language, which permits the use of complex arithmetic and results in shorter programs. Program CMER computes relative phase Δ and relative amplitude parameter ψ for reflection from bare surfaces from given values of the optical constants n and k . Program QMOC computes complex optical constants from relative phase and amplitude or ellipsometer readings of polarizer and analyzer circles in different zones. Two other programs have been modified to permit the use of ellipsometer circle readings, rather than relative phase and amplitude parameters as input and output variables. Program FILM computes the thickness and complex refractive index of a single, absorbing film on an absorbing substrate from ellipsometer readings in different zones. Program DPLOT calculates and plots ellipsometer readings for films of given optical constants and thickness.

Programs for eliminating the effect of birefringent cell windows from ellipsometer measurements, together with the effect of imperfections in polarizers and compensators, are being developed.

d. Optical Interference in Thin Films

Charles R. Brown and Rolf H. Müller

As a test of generalized interference colors which have been computed previously,¹ the thickness of films derived from interference colors will be compared to thickness determinations which do not depend on the optical properties of the film or substrate.

Thin film-substrate combinations are prepared by vapor deposition on chemically and thermally cleaned glass slides in a

residual gas pressure of 10^{-6} Torr. To ensure low reactivity with ambient gases and to cover the widest possible range of optical phase changes due to reflection, Ag, Cr and Si are used as substrate materials. MgF₂ and cryolite were chosen as the film materials. These materials are transparent in the visible and are well characterized optically and mechanically. To avoid contamination of the substrate, its deposition (on glass) in the vacuum chamber is followed immediately by the deposition of the thin film. The substrate is radiantly heated from a hot tungsten wire. Substrate and source temperatures are measured by Pt-Rh thermocouples.

White light interference colors for different angles of incidence are recorded photographically using a positive, 35 mm color film. In addition, interference spectra are recorded photometrically using a previously-built ratio-recording double beam spectrophotometer.¹ Local thin film thickness is then derived (a) from the interference colors and (b) from the interference spectrum.

Results thus obtained are compared with step height determinations at the edge of the film by two other techniques: (1) a mechanical stylus instrument and (2) interference microscopy. In addition, ellipsometry will be used as an overall check.

1. J. H. Turney, Profiles of Supermeniscus Electrolyte Films on Partially Submerged Gas Electrodes (M. S. thesis), LBL-171, August 1971.

2. RESEARCH PLANS FOR CALENDAR YEAR 1973

Rolf H. Müller

Measuring techniques, now sufficiently developed for the interferometry of mass-transfer boundary layers, will be used for the detailed study of convective transport in electrolysis.

The automatic ellipsometer will be used for the study of transient anodic surface layers on metals. New computational procedures for the efficient interpretation of ellipsometer measurements and the elimination of the effect of optical imperfections will be developed.

Tests of the effect of phase change in optical reflection from a metal substrate,

on the derivation of film thickness from interference colors, will be completed.

The effect of microscopic surface roughness on mass transfer with high flow rates in narrow channels will be investigated (see Paper 2a of Prof. Tobias' section).

The propagation of electrical breakdown phenomena will be studied in the investigation of anodic oscillations (see Paper 2b of Prof. Tobias' section).

LBL reports

1. K. W. Beach, R. H. Muller, and C. W. Tobias, Light Deflection Effects in the Interferometry of One-Dimensional Refractive Index Fields, LBL-1102, Sept. 1972 (submitted to J. Opt. Soc. of America).

2. R. H. Muller, Double Beam Interferometry for Electrochemical Studies, chapter in book Advances in Electrochemistry and Electrochemical Engineering, Vol. 9 (to be published by Interscience); LBL-115 Rev., March 1972.

3. 1972 PUBLICATIONS AND REPORTS

Rolf H. Muller and Associates

Journals and books

1. K. W. Beach, R. H. Muller, and C. W. Tobias, A One-Dimensional Focusing Critical Angle Refractometer for Mass Transfer Studies, Rev. Sci. Instr. 43, 925 (1972) (LBL-153).

John Newman, Principal Investigator

1. ANALYSIS OF POROUS ELECTRODES WITH SPARINGLY SOLUBLE REACTANTS

John S. Dunning, Douglas N. Bennion, and John Newman

The galvanostatic operation of flooded porous electrodes employing metal/metal salt couples was analyzed. A model was developed for a single circular pore configuration which accounts for the effects of differing equivalent volumes of the solid reactants. The model also includes effects of variation in solution properties and effects of complexing of the sparingly soluble salt with the bulk electrolyte anion. Overpotential was computed as a function of time for the solid-film and solution-diffusion versions of the model. The solid-film model shows a linear overpotential-time relationship and nearly uniform current distribution. The solution-diffusion model shows a variety of overpotential-time curves, based on different physical parameters, and may generate extremely nonuniform current distributions, often with maxima inside the pore. These persistent nonuniform current distributions are important in terms of the analysis of cycling behavior.

2. POTENTIAL DISTRIBUTION IN AXISYMMETRIC MERCURY-POOL ELECTROLYSIS CELLS AT LIMITING CURRENT

John Newman and Jackson E. Harrar

Uniformity of potential at the working electrode has become an important criterion in the design of electrolysis and coulometry cells. Deviations of the actual electrode potential from the desired control potential may cause significant errors in coulometry and unwanted product distributions in electro-organic syntheses.

Because excursions of the working electrode potential are minimized, the preferred configuration of a mercury-pool type cell is the axisymmetric arrangement in which the counter electrode separator is placed concentrically above the pool. When the separator is parallel to the pool, and of nearly the same diameter, a virtually uniform potential distribution should be achieved, and has been experimentally realized. For cells in which the separator is considerably smaller in diameter than the pool, however, a

significantly nonuniform distribution may result. The degree of nonuniformity has been analyzed, and the problem of optimal location for the reference electrode has been discussed.¹

1. J. Newman and J. E. Harrar, Potential Distribution in Axisymmetric Mercury-Pool Electrolysis Cells at the Limiting Current, LBL-1155, September 1972.

3. MASS TRANSFER TO A NON-NEWTONIAN FALLING FILM

Charles Mohr and Michael C. Williams

The Ellis rheological model was used to describe the hydrodynamics of a falling non-Newtonian liquid film. A perturbation analysis for the two resulting parameters in the convective diffusion equation for diffusion of a gas into the film resulted in a hierarchy of equations which were readily solvable via computer. Results indicate that this is an accurate and economical way to allow for variation of system and fluid parameters in those situations requiring precise knowledge of the effect of the non-parabolic velocity profile.

4. MASS TRANSFER IN CYLINDRICAL COUETTE FLOW

Charles Mohr and John Newman

Theoretical equations for mass transfer to a section of the inner electrode for laminar cylindrical couette flow were derived and analytical solutions obtained. The effects of curvature, the nonlinear nature of the velocity profile, and elliptic effects at the ends of the diffusion layer were included to extend the results of a previous treatment.¹ The mass transfer Nusselt number was found to be a function of the Péclet number and the ratio of electrode length to inner cylinder radius.² Corrections due to elliptic effects dominated for short electrodes, but as electrode length approached the inner cylinder radius, curvature and velocity profile corrections became predominant. For typical liquid systems of interest, these corrections totaled less than 10%.

1. D. R. Gabe and D. J. Robinson, *Electrochimica Acta*, 17, 1121 (1972).
2. C. Mohr and J. Newman, LBL-1141, September 1972.

5. CORROSION OF AN IRON ROTATING DISK

Nader Vahdat and John Newman

The corrosion rate of iron rotating disks was predicted by calculating the current and potential distributions on the surface of the disk.^{1,2} The results show that the surface towards the center of the disk is corroded at the maximum rate, while the edge of the disk remains almost unattacked, due to passivation, in agreement with experimental observations. The effect of different parameters on the corrosion behavior was also considered.

1. N. Vahdat and J. Newman, LBL-896, July 1972.
2. N. Vahdat, M. S. thesis, LBL-873, June 1972.

6. MASS TRANSFER COEFFICIENT IN POROUS FLOW THROUGH ELECTRODES

Harry H. Yip, John Newman, and Peter Appel

The flow system used previously has been modified extensively. The electrolyte solution now is pumped continuously from a reservoir through a microfilter (0.2μ pores) to an over flow tank, from where it flows back to the reservoir.

The flow system is contained in a constant-temperature hood to minimize natural convection effects.

Flow disturbances at the entrance and exit of the packed bed have been diminished by containing the packing material between two fritted glass disks. Also, the current collector--previously a stainless steel plate with holes drilled in it--has been replaced with a stainless steel screen.

7. THE RADIALLY DEPENDENT CONVECTIVE WARBURG PROBLEM

John Newman and Peter Appel

Using an alternating concentration jump on

the surface of a rotating disk as a boundary condition for the convective diffusion equation, the time-dependent concentration distribution in radial and normal direction has been solved numerically. This solution agrees well with asymptotic solution for both close to and far away from the concentration jump.

The solution far away from the concentration jump agrees with values obtained for the radially independent solution.

8. A COMPOSITE EXPANSION FOR THE WAKE JUST BEHIND A FLAT PLATE

John Newman and D. Theodore Scalise

The fluid flow in the boundary layer adjoining all solid surfaces presents a singular-perturbation problem. A change in the boundary conditions may generate additional regions in which different treatments are necessary.

This singular-perturbation property is exhibited in Goldstein's¹ classical investigation of a fundamental problem of fluid mechanics--that of determining the fluid velocity distribution in the near-wake boundary layer of a flat plate. Using one set of coordinate variables in the series expansion, he found an approximate solution valid only for the inner region near the plane of the plate; with another set of coordinate variables he found an approximate solution valid only for the outer region, the part of the boundary layer lying farther from the plane of the plate.

In this contribution,² we construct a uniformly valid expansion to the classical near-wake problem, using the method of matched asymptotic expansions. This is compared with Goldstein's inner and outer solutions at a downstream distance of half the plate length. The great improvement is evident in the fact that whereas the old solutions are discontinuous in the central region, the new solution is continuous throughout the whole flow domain, merging to the old solutions at both extremities.

1. S. Goldstein, Concerning Some Solutions of the Boundary Layer Equations in Hydrodynamics, *Proc. Cambridge Phil. Soc.* 26, 1-30 (1930).
2. John Newman and D. Theodore Scalise, An Improved Solution to the Classical Near-Wake Boundary -Layer Problem, March 1973, LBL-1430.

9. MASS TRANSFER TO A PLANE BELOW A ROTATING DISK AT HIGH SCHMIDT NUMBERS

Robert V. Homsy and John Newman

The Lighthill transformation is used to determine¹ the rate of mass transfer at high Schmidt numbers to a disk imbedded in a stationary plane below a rotating disk. This diffusion-layer solution breaks down near the center and leading edge of the mass-transfer disk. Solutions in these regions have been obtained previously^{2,3} and are applied to this problem. A uniformly valid composite solution for the local Nusselt number is determined along with an expression for the average mass-transfer rate to the disk.

An electrochemical experiment has been designed to measure the rate of mass transfer to the plane, using a copper deposition reaction at limiting current.

1. Robert V. Homsy and John Newman, Mass Transfer to a Plane Below a Rotating Disk at High Schmidt Numbers, LBL-1420, January 1973.
2. John Newman, Mass Transfer to the Rear of a Cylinder at High Schmidt Numbers, Ind. Eng. Chem. Fund. 8, 553-557 (1969).
3. John Newman, The Fundamental Principles of Current Distribution and Mass Transport in Electrochemical Cells, in Electroanalytical Chemistry, Vol. 6, edited by A. J. Bard (Marcel Dekker, New York, 1973), pp. 187-352.

10. THE TRANSIENT RESPONSE OF A DISK ELECTRODE

Kemal Nişancıoğlu and John Newman

The current-interruption technique is a commonly used method for the assessment of the ohmic drop in the solution in electro-analytical applications. One question arises as regards the physical significance of the ohmic drop measured by such techniques.¹ Another question is more particular to the disk electrode, which exhibits a nonuniform current distribution,² and the manner by which the charge decays after the interruption at the double layer poses a nonelementary problem.

A mathematical model is proposed to treat the transient response of a disk electrode to changes in the applied current³ and applied potential.⁴ Analyses reduce to well-defined boundary-value problems, which yield solutions in terms of newly defined eigenfunctions.

The results allow the determination of time constants characteristic of decay due to an electrode reaction and due to a redistribution of charge within the double layer during the transient process.

1. John Newman, Ohmic Potential Measured by Interrupter Techniques, J. Electrochem. Soc. 117, 507-508 (1970).
2. John Newman, Resistance for Flow of Current to a Disk, *ibid.*, 113, 501-502 (1966).
3. Kemal Nişancıoğlu and John Newman, The Transient Response of a Disk Electrode, LBL-1109, July 1972.
4. Kemal Nişancıoğlu and John Newman, The Transient Response of a Disk Electrode with Controlled Potential, LBL-1173, October 1972.

11. CURRENT DISTRIBUTION AT A ROTATING SPHERE BELOW THE LIMITING CURRENT

Kemal Nişancıoğlu, Robert V. Homsy, and John Newman

The rotating spherical electrode finds use in electrochemistry because it exhibits a uniform primary-current distribution and thus is applied in current-step methods¹ and high-rate dissolution studies.² The limiting-current distribution for this geometry has recently been calculated,^{2,3} and the distribution below the limiting current is also of interest.

The numerical method, which has been applied effectively to a number of electrode geometries in the past⁴⁻⁷ is adapted and successfully tested for the rotating sphere. A number of case problems need to be worked out on the computer before reporting the results.

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3. John Newman, Mass Transfer to a Rotating Sphere at High Schmidt Numbers, *ibid.*, 119, 69-71 (1972).
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5. John Newman, The Diffusion Layer on a Rotating Disk Electrode, *ibid.*, 114, 239 (1967).

6. W. R. Parrish and John Newman, Current Distribution on a Plane Electrode below the Limiting Current, *ibid.*, 116, 169-172 (1969).
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12. RESEARCH PLANS FOR CALENDAR YEAR 1973

John Newman

The mass-transfer coefficient for packed beds at low Reynolds numbers will be measured by the electrochemical reduction of ferri-cyanide ion. The local mass-transfer coefficient for turbulent flow on a rotating disk will be studied by electrochemical deposition of copper. Calculations should reveal the effect of ionic migration on limiting currents in turbulent-flow situations. Lead will be removed from a $PbSO_4$ saturated sulfuric acid solution by electrochemical deposition in a flow-through porous electrode.

Experiments are contemplated for measuring the time constant for transient current or potential changes for a disk electrode in the absence of concentration variations. A related effort involves the calculation of the alternating-current impedance for a disk electrode with consideration of concentration variations and the nonuniform ohmic potential drop to the disk. A rotating disk can also establish a convective flow pattern on the bottom of the cell. The mass transfer to this plane will be studied by the electro-deposition of copper.

The analysis of a rotating ring-disk system with nonuniform current densities shows promise of a successful and fruitful completion. Thermodynamic data for binary systems will be used to predict the thermodynamic properties of ternary solutions. Expressions for calculating virial coefficients at low temperatures will be worked out, using Lennard-Jones type interaction potentials. Studies may be begun on electrophoresis and electro-osmosis.

13. 1972 PUBLICATIONS AND REPORTS

John Newman and Associates

Journals

1. J. Newman, Mass Transfer to a Rotating Sphere at High Schmidt Numbers, *J. Electrochem. Soc.* 119, 69-71 (1972) (UCRL-20599).

2. W. Tiedemann and J. Newman, Growing Porous Layers, *J. Electrochem. Soc.* 119, 186-188 (1972).
3. W. Smyrl and J. Newman, Detection of Nonuniform Current Distribution on a Disk Electrode, *J. Electrochem. Soc.* 119, 208-212 (1972) (UCRL-20380).
4. W. Smyrl and J. Newman, Ring Disk and Sectioned Disk Electrodes, *J. Electrochem. Soc.* 119, 212-219 (1972).
5. J. Newman, Book Review: Ionic Interactions edited by S. Petrucci, *Science*, 175, 1451-1452 (1972).
6. D. Bennion and J. Newman, Electrochemical Removal of Copper Ions from very Dilute Solutions, *J. Appl. Electrochem.* 2, 113-122 (1972).

Paper presented

1. J. Newman, Corrosion of Iron Rotating Disks, lecture at Sandia Laboratories, Albuquerque, New Mexico, July 24, 1972.

LBL reports

1. J. Newman and W. Smyrl, Fluid Flow in a Propagating Crack, LBL-824, April 1972.
2. N. Vahdat, The Corrosion of Iron Rotating Disks, M. S. thesis, LBL-873, June 1972.
3. N. Vahdat and J. Newman, Corrosion of an Iron Rotating Disk, LBL-896, July 1972.
4. W. Tiedemann, J. Newman, and D. Bennion, The Error in Measurements of Electrode Kinetics Caused by Nonuniform Ohmic Potential Drop to a Disk Electrode, LBL-890, June 1972.
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6. C. Mohr, Jr. and J. Newman, Mass Transfer in Cylindrical Couette Flow, LBL-1141, September 1972.
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10. R. Homsy and J. Newman, Mass Transfer to a Plane below a Rotating Disk at High Schmidt Numbers, LBL-1420, December 1972.

11. K. Nişancıoğlu and J. Newman, Diffusion in Aqueous Nitric Acid Solutions, LBL-1428, December 1972.

12. D. Scalise and J. Newman, An Improved Solution to the Classical Near-Wake Boundary Layer Problem, LBL-1430, December 1972.

Translations

1. J. Besenhard and H. P. Fritz, Investigation of the Behavior of Graphite Electrodes in Nonaqueous Electrolytes, Z. Naturforsch. 26B, 1225-1229 (1971). Translated by R. Homsy, UCRL-Trans.-1476, April 1972.

2. B. Kabanow and A. Frumkin, On the size of Electrolytically Generated Gas Bubbles, Z. Physik. Chem. 165A, 433-452 (1933) and 166A, 316-317 (1933). Translated by J. Newman, UCRL-Trans-1485, September 1972.

3. E. Levart and D. Schuhmann, On the Diffusional Impedance for a Rotating Disk Electrode in the Range of Very Low Frequencies, Coll. Czech. Chem. Comm. 36, 866-876 (1971). Translated by C. Mohr, UCRL-Trans-1484, August 1972.

D. PHYSICAL CHEMISTRY

Leo Brewer, Principal Investigator

1. THERMODYNAMIC PROPERTIES OF THIRD AND FOURTH GROUP TRANSITION METALS WITH PLATINUM GROUP METALS

John P. Stiga and Garry B. Bullard

Vaporization studies are in progress to establish the dependence of Gibbs energy upon concentration in solutions of strongly interacting metals. It is planned also to initiate experiments with high temperature cells, using solid electrolytes.

2. APPLICATION OF THE REGULAR SOLUTION THEORY TO METALLIC SOLUTIONS

John P. Stiga

A modification of the regular solution theory that uses promotion energies to obtain cohesive energies is being tested for metallic solutions that do not have strong interactions due to electron transfers.

3. OPTICAL PUMPING IN RARE GAS MATRICES

Dan D. Jensen

In previous work¹ on the spectrum of Mg in rare gas matrices, it was not possible to identify some features, and it was suggested that they might be due to absorption from optically pumped levels of Mg. Absorption experiments with and without the wavelength required for the proposed optical pumping gave the same absorption features. Thus they could not be due to optical pumping and are probably Mg₂ features.

1. L. Brewer and J. Wang, *J. Mol. Spectr.* **40**, 95-102 (1971).

4. COMPILATION OF TERNARY PHASE DIAGRAMS

Shih-Ger Chang and John Chipman

Preparation of updated ternary phase diagrams for the Metals Handbook of the American Society for Metals has been largely completed and should be finished early in 1973.

5. SOLUBILITIES OF INTERMETALLIC COMPOUNDS IN IRON

Leo Brewer

Work is progressing on the compilation of data on solubility of intermetallic precipitates in iron and the prediction of behavior of all the metallic elements when dissolved in iron.

6. THERMODYNAMIC PROPERTIES OF Mo AND ITS COMPOUNDS

Leo Brewer

Work is proceeding on this compilation of experimental data and predicted values.

7. THERMODYNAMIC PROPERTIES AND PHASE DIAGRAMS OF THE ALLOY SYSTEMS OF THE LANTHANIDE AND ACTINIDE METALS

Leo Brewer

The calculations of the phase diagrams of the alloy systems of the lanthanides and actinides are progressing and should be completed by the end of 1973.

8. RESEARCH PLANS FOR CALENDAR YEAR 1973

Leo Brewer

The studies of vaporization of transition metal alloys will be continued and be supplemented by high temperature electromotive force measurements.

Work on thermodynamic and phase diagram compilations and calculations will be continued for some ternary phase diagrams, systems of molybdenum and iron with all elements, and systems of the lanthanides and actinides with all elements.

In addition, it is expected that manuscripts on the low-lying electronic states of CaO and the transition probability of the Swan bands of C₂ will be completed. If support can be obtained, it is planned to do additional work on the matrix isolation of oxides of Mg and Ca.

9. 1972 PUBLICATIONS AND REPORTS

Leo Brewer and Associates

Journals and books

1. Leo Brewer, Bibliography on the High Temperature Chemistry and Physics of Materials, Part II. A. Spectroscopy of Interest to High Temperature Chemistry; B. Reactions Between Gases and Condensed Phases. Edited by M. G. Hocking, Vol. 16, Nos. 1, 2, 3, 4 (1972).

2. Leo Brewer, Relevancy of Research, J. Electrochem. Soc. 119, 7-12C (1972) (LBL-195).

3. Leo Brewer and J. L. Wang, Infrared Absorption Spectra of Isotopic Ozone Isolated in Rare-Gas Matrices, J. Chem. Phys. 56, 759-762 (1972) (LBL-141 Rev.).

4. Leo Brewer and C. Chang, Matrix Isolation of Pb and Pb₂, J. Chem. Phys. 56, 1728-1740 (1972) (LBL-149).

5. Leo Brewer and C.-A. Chang, Electrical Conductivities of Pb/Xe and Pb/SF₆ Films, J. Phys. Chem. Solids 33, 457-459 (1972) (UCRL-20581).

6. Leo Brewer and Joel Tellinghuisen, Quantum Yield for Unimolecular Dissociation of I₂ in Visible Absorption, J. Chem. Phys. 56, 3929-3938 (1972) (LBL-400).

7. Leo Brewer and J. Ling-Fai Wang, Ground State of Gaseous CaO; a Study of the Matrix Spectra of Ca and CaO, J. Chem. Phys. 56, 4305-4309 (1972) (LBL-445).

8. Leo Brewer, The Complexity of High Energy Chemistry, Int. J. Sulfur Chem., Part B, Vol. 7, No. 1, pp. 31-35 (1972) (LBL-132).

9. K. Wieland, J. B. Tellinghuisen, and A. Nobs, The Band Systems E + X (2530-2740Å) of I₂I₂ and I₂I₂, and the Corresponding System E + B of Br₂ and Cl₂, J. Mol. Spectr. 41, 69-83 (1972) (LBL-860).

10. D. D. Jensen, The Absence of Optical Pumping in Matrix-Isolated Magnesium, J. Mol. Spectr. 43, 472-473 (1972) (LBL-803).

LBL reports

1. Chin-An Chang, Temperature Dependence of Matrix Shifts, LBL-434 Rev., Feb. 1972.

2. Shih-Ger Chang, High Temperature Spectroscopy and Thermodynamics of Titanium Oxide and Vanadium Oxide (Ph.D. thesis), LBL-450, March 1972.

3. Leo Brewer and Paul R. Wengert, Transition Metal Alloys of Extraordinary Stability; an Example of Generalized Lewis-Acid-Base Interactions in Metallic Systems, LBL-807, March 1972 (submitted to Metallurgical Trans.).

4. Leo Brewer, Transition Metal Alloys--A Chemist's View, 18th Annual Conference on Magnetism and Magnetic Materials, Denver, Col. Nov. 28, 1972. (To be published in American Institute of Physics Conference Proceeding Series.) LBL-1424, Nov. 1972.

Charles B. Harris, Principal Investigator

1. EXCITED TRIPLET STATES IN MOLECULES AND MOLECULAR CRYSTALS

Charles B. Harris

Using new techniques recently developed in these laboratories which utilize simultaneous optical and microwave pumping (Phosphorescence-Microwave-Double-Resonance Spectroscopy), we are studying molecular properties of excited triplet states and the dynamics of excited state energy transfer (excitons) in molecular crystals. In oversimplified terms, luminescence from excited triplet states of "isolated" molecules or mobile electronic states, excitons, is monitored while a microwave field changes the orientation of the electron spin in the triplet state. This causes a change in the intensity or polarization of the emission and forms the basis for a technique capable of detecting as few as 10^4 molecules in excited states. Many features of triplet states can be studied by analyzing the microwave transitions and the triplet phosphorescence. These include electron distributions, nuclear-electron interactions, excited state orbital symmetries, molecular distortions in excited states and, finally, the rates, routes, and mechanisms of inter- and intramolecular energy transfer. In addition we are investigating relatively unexplored but very important aspects of excited states involving molecular processes that occur on a time scale of 10^{-9} to 10^{-12} seconds. These are all fundamental in nature and include such things as the primary mechanism in energy migration, radiationless relaxation phenomena, and electron and/or proton transfer between molecules. A variety of mechanisms have been postulated and theoretically developed for these processes; however, because of the extraordinary short time scale of the processes, few have been studied. Using Picosecond (10^{-12}) Laser Spectroscopy certain key aspects of the above phenomena are being experimentally investigated in our laboratory. In effect, a picosecond laser pulse is used to generate molecules in excited states and then it is used to follow spectroscopically the time development of the system under investigation. Since it is possible to obtain the complete spectra of molecules in $\sim 3 \times 10^{-13}$ second using picosecond techniques, the primary events and time dependent changes associated with excited states, such as energy transfer, radiationless transitions, and the coherence associated with oscillating electric dipolar states in molecules can be systematically investigated.

2. COHERENT ENERGY MIGRATION IN MOLECULAR SOLIDS

Charles B. Harris

In order to describe the dynamics of exciton migration in the Frenkel limit, the electronic states, the phonon states, and phonon-exciton coupling must all be explicitly considered in terms of the crystal states. Indeed, it is the latter interaction that determines the primary mechanism responsible for electronic energy transfer in solids at both high and low temperatures. At low temperature the density of phonon states becomes sufficiently small that scattering between the exciton wave vector states k by the phonons is expected to be much less frequent than energy migration from lattice-site to lattice-site. In the limit that the time between scattering events approaches the radiative or radiationless lifetime of the excited electronic state, a Frenkel exciton can be thought of as localized excitation propagating coherently as a wave packet at a velocity characteristic of both its energy and a linear combination of the crystal k states. This velocity is termed the group velocity and is given by

$$V_g(k) = (2\pi/\hbar)(d\epsilon/dk) \quad (1)$$

and for a one dimensional crystal, $\epsilon(k)$

$$\epsilon(k) = E^0 + 2\beta \cos ka \quad (2)$$

is the band dispersion associated with translational equivalent interactions along a direction $\hat{a}$. E^0 is the electronic energy of the localized molecular excited state while β is the effective intermolecular interaction in the nearest neighbor approximation. The distance $\lambda(k)$, which an exciton propagates in a coherent fashion without changing either its direction or velocity is given by the lifetime of the coherent state, $\tau(k)$, times the group velocity of the wavepacket:

$$\lambda(k) = V_g(k) \cdot \tau(k) \quad (3)$$

$\lambda(k)$ is thus equivalent to a mean-free path and $\tau(k)$ corresponds to a coherence time for the wave vector state k . From a dynamical point of view the important feature of coherent migration is that excitons can propagate in the crystal at a variety of velocities and a variety of distances depending upon the k states populated. For the case under consideration the group velocity is zero at the top and bottom of the

band ($k = 0$ and $\pm\pi/a$) but $8\pi\hbar/h$ at the center of the band ($k = \pm\pi/2a$). The extent to which these states contribute to the propagation of electronic energy in a given situation is determined explicitly by the population distribution in the band. For a thermal distribution, the number of excitons $N(k)$ propagating with a velocity $V_g(k)$ is proportional to the density of states $\rho(\epsilon)$ times the Boltzmann factors:

$$N(k) \propto \rho(\epsilon) \cdot \exp[-\epsilon(k)/kT]. \quad (4)$$

The importance of coherent exciton migration is perhaps best illustrated by comparing it to the high temperature diffusion limited random walk process. High temperature is characterized by a density of populated phonon or localized vibrational states sufficient to limit the coherence lifetime of an exciton k state by scattering it to other states in the band. When this causes a change of k at a rate comparable to intermolecular energy exchange, the delocalized wave vectors of the crystal are no longer good wavefunctions for times exceeding $(\beta)^{-1}$ and the proper description of the exciton becomes the Fourier transform function of the exciton k states. In this limit the exciton, on the average, changes its velocity and direction at every lattice site and propagates in a diffusion limited random walk manner. For one-dimensional propagation the velocity of migration of the exciton is simply an RMS average velocity, and is proportional to $(\beta)^{1/2}$. Consider, for example, a molecular crystal with nearest neighbor molecules having an effective intermolecular interaction of 1 cm^{-1} and a lattice spacing of $4 \text{ \AA}$. The diffusion limited exciton velocity is 10^{-2} cm/sec while coherent states have a group velocity at the center of the band of 10^4 cm/sec . The mean-free path for diffusion is $4 \text{ \AA}$; however, for coherent states at $k = \pm\pi/2a$ it is

$$\lambda(k = \pm\pi/2a) = (8\pi\hbar/h) \cdot \tau(k = \pm\pi/2a). \quad (5)$$

It is self-evident that the coherence length can approach macroscopic dimensions if phonon-exciton scattering is weak [i.e., $\tau(k)$ is long] and the excited states are long-lived (e.g., triplet states). In practice this is only achieved at very low temperatures where the distribution of phonon states approaches the $T=0$ limit. At intermediate temperatures the principal limitation of $\tau(k)$ is phonon-exciton scattering. In such cases an exciton initially in a k state scatters to other k' states via phonon interactions in a time short compared to the radiative or radiationless lifetime, but in a time long compared to intermolecular exchange. As a result the coherence time is shortened, the mean-free path or coherence length is reduced, and the

individual k states acquire a width $\Gamma(k)$, given by the reciprocal of the coherence lifetime of the individual k states. $\Gamma(k)$ is given by

$$\Gamma(k) = [\tau(k)]^{-1} = \sum_{k'} (\tau_{kk'})^{-1}, \quad (6)$$

where $\tau_{kk'}$ is the probability of an exciton initially in the k th state scattering via phonon-exciton interactions to a final state k' .

Thus, a proper description of the dynamics of exciton migration must include in addition to the stationary states of the crystal (a) the group velocities of excitons, (b) the population distribution over the k states of the band, and (c) the coherence times for the individual k states and hence an explicit model for phonon-exciton scattering. This description views the exciton as executing a random walk migration in a time on the order of the coherence lifetime and allows for long-range propagation via coherent migration in between scattering events.

From an experimental point of view, this model requires that careful attention be given to the relationship between the correlation time associated with exciton migration and the time scale of the particular experimental approach being employed. If, for example, the experimental correlation time, which is on the order of the reciprocal of the radiation field, is much shorter than $\tau(k)$ (as is the case for optical absorption), only manifestations of the coherent model are apparent from the data. Similarly, when the experimental correlation time is longer than $\tau(k)$ for all k , only the random walk processes are displayed. A reliable measure of phenomena connecting coherent migration and diffusion limited migration, such as phonon-exciton scattering, $V_g(k)$ and $\lambda(k)$, can only be determined when the experimental correlation time is on the order of $\tau(k)$. It is on this basis that the following outlined experiments provide a direct probe into the dynamics of triplet excitons.

3. ELECTRON SPIN RESONANCE ABSORPTION IN COHERENT TRIPLET EXCITON STATES

Charles B. Harris

An electron spin resonance theory for excitons in a one-dimensional crystal composed of translationally equivalent molecules has been developed. The excited triplet band is derived from intermolecular exchange coupling

between the ground singlet and excited triplet states and is restricted to nearest neighbor interactions. Furthermore, a Boltzmann distribution over the band was assumed. In zero magnetic field the triplet band is split into three parallel bands by electron spin dipolar repulsions. The spin sublevel bands are designated as τ_x , τ_y , and τ_z and correspond to states in which the electron spins are correlated in the x , y , and z molecular axes respectively. Electron spin transitions between any two spin sublevels are independent of k in zeroth order since the spin Hamiltonian is k independent. In first order, however, selective spin-orbit coupling between excited singlet molecular states and individual molecular spin sublevels of the triplet results in a k -dependent contribution to the zero-field band splitting and hence a k -dependent electron spin band-to-band transition between magnetic sublevels. The k dependence of the Larmor frequency, ω_0^k , is given by

$$\omega_0^k = \xi' [2\beta \cos ka], \quad (7)$$

where ξ' is a factor related to the details of spin-orbit coupling.

The proper representation for electron spin resonance absorption in terms of the Bloch formalism is a set of Bloch equations, one for each k state in the band, whose frequency components ω_0^k are coupled by phonon-exciton scattering. In the rotating frame the presence of a weak oscillating rf field of the form

$$H(t) = -\gamma H_1 \cdot \hat{S}_y \cos \omega t \quad (8)$$

connecting τ_x with τ_z via the electron spin operator $\hat{S}_y$ results in an in-phase, u , and out-of-phase, v , component of a complex moment, G , given by

$$G_k = u_k + i v_k. \quad (9)$$

Modified Bloch equations were constructed from the complex moments of each k state that include the effects of phonon-exciton scattering phenomenologically through the scattering rates $(1/\tau_{kk'})$. The $(2k+1)$ equations are:

$$dG_k/dt + [1/T_2(k) - i(\omega_0^k - \omega)]G_k = -i\gamma H_1 N(k) + \sum_{k'} [G_{k'}/\tau_{k'k} - G_k/\tau_{kk'}], \quad (10)$$

where $N(k)$ is given by Eq. (4). $T_2(k)$ is the homogeneous spin-spin relaxation time for the k th exciton state. $1/\tau_{kk'}$, or the probability

per unit time for an exciton being scattered by a phonon from k to k' , is displayed as a "golden rule" rate

$$1/\tau_{kk'} = \rho_e(k') \sum_{\lambda, q, q'} \rho_p(q') \exp[-E^\lambda(q)/kT] \rho_p(q) \times | \langle kq | \mathcal{H}_{ep}^\lambda | k'q' \rangle |^2 \delta(k+q, k'+q'). \quad (11)$$

$\rho_e(k')$, $\rho_p(q')$, and $\rho_p(q)$ are the exciton (subscript e) or phonon (subscript p) density of states functions evaluated at the energy of the wave vector k' , q' , or q respectively. λ is the index which runs over the phonon branches and $E^\lambda(q)$ is the energy of the q th wave vector of the phonon branch. The sum over phonon states q and q' is restricted to collisions that conserve both the total energy and momentum of the initial and final exciton-phonon states $\langle kq |$. $\mathcal{H}_{ep}$ is the exciton-phonon coupling Hamiltonian. In weak oscillating rf fields and steady state ($dG_k/dt = 0$) the electron spin resonance line shape function, $g(\omega)$, is given by:

$$g(\omega) = \text{Im} \sum_k G_k. \quad (12)$$

The function $g(\omega)$ was easily solved in two limits. The first, termed the strong scattering case, occurs when $(\omega_0^k - \omega_0^{k'})/\tau_{kk'} \ll 1$ and yields a homogeneously narrowed line centered at $k = \pm\pi/2a$ at high temperatures and corresponds to the random walk limit. The second, when $(\omega_0^k - \omega_0^{k'})/\tau_{kk'} \gg 1$, corresponds to the coherent limit in which phonon-exciton scattering causes a change in the exciton states on a time $(\tau_{kk'})$ slow compared to the differences in the Larmor frequencies $(\omega_0^k - \omega_0^{k'})$. In such cases the individual k states of the triplet band can be sampled by the rf field. Assuming phonon-exciton scattering to be uniform in k , i.e., $\tau_{kk'}$ are equal for all k and k' , the electron spin resonance absorption $g(\omega)$ is the sum of $(2k+1)$ independent Lorentz lines each centered at ω_0^k and weighted by the number of excitons occupying the state k with group velocity $V_g(k)$. The width of each Lorentz has a contribution from both a finite coherence lifetime $\tau(k)$ and the homogeneous line with parameter $T_2(k)$. When a thermal distribution characterizes the triplet band

$$g(\omega) = \frac{\delta}{\pi} \int_0^{\pi/a} \frac{\exp[4\beta(1 - \cos ka)/kT]}{[\omega + \frac{\delta}{\Delta T} \cos ka]^2 + \delta^2} dk. \quad (13)$$

$\Delta\epsilon_{ST}$ is related to spin orbit coupling, T is temperature, δ is the half width at half height of an individual k state electron spin transition and is a measure of $\tau(K)$.

Some specific features of Eqs. (10) and (13) are that: (a) The Larmor frequencies are directly related to band energy insofar as a prescribed ω_0 couples the spin sublevels of an exciton whose energy is $\epsilon(K)$. (b) The intensity of the transition is directly related to the density of states function times a Boltzmann factor. The relative heights of the transition maxima at $\sim k = 0$ and $\pm\pi/2a$ results from the Boltzmann factor evaluated at the maxima in the density of states function at the top and bottom of the band and thus gives a value for the band width. (c) The broadening function δ gives an estimate of the phonon-exciton scattering, and hence a measure of the coherence length $\lambda(K)$ and insight into the mechanism of phonon-exciton scattering. The dependence of $g(\omega)$ on T via $(T/K)^{-1}$ might, for example, allow linear and quadratic phonon-exciton coupling to be distinguished experimentally. (d) The overall width of the $g(\omega)$ is determined by the spin-orbit coupling parameter $\Delta\epsilon_{ST}$, hence the selectivity of spin-orbit coupling to the triplet spin sublevels can be determined. (e) The microwave field selectively perturbs the electron spin of excitons whose group velocity is $V_g(K)$, and therefore the k dependence of other processes such as the dynamics of trapping, exciton-exciton annihilation etc. can be potentially studied in the coherent limit. Thus, electron spin resonance provides a direct technique for measuring band structures, intramolecular exchange interactions, phonon-exciton scattering, and other related phenomena.

4. EXCITON-TRAP INTERACTIONS IN THE COHERENT AND INCOHERENT LIMITS

Michael D. Fayer and Charles B. Harris

At liquid He temperature, phosphorescent emission from organic molecular crystals in general comes from low energy traps in the lattice although in some molecules, such as 1,2,4,5-tetrachlorobenzene and 1,4-dibromonaphthalene, exciton emission is also observed. The intensity of trap emission is highly temperature dependent in certain temperature regions. This temperature dependence is found to be explicable in terms of a theoretical framework, which includes the method of energy transport in the crystal and the magnitude and sign of the intermolecular interactions which give rise to the exciton bands in the crystal.

Initially the problem was considered for an ensemble consisting of one-dimensional exciton bands and traps of only one energy. The trap intensity is given by $I_{\text{trap}}(T) = K_{\text{trap}} N_{\text{trap}} = K_{\text{trap}} N_{\text{total}} P_{\text{trap}}(T)$, where K_{trap} is the radiative rate constants, N_{trap} is the trap population, and N_{total} is the total excited state population of the system. Since an excitation must either be in the exciton bands or in the traps, the trap population is equal to the total population times $P_{\text{trap}}(T)$, the probability that an excitation is in a trap. The number of energy levels in a one-dimensional exciton band is equal to the number of identical molecules in the linear chain forming the exciton. These energy levels are labeled by the quantum number K, and the energy as a function of k is given by $E(K) = 2\beta \cos ka$, where β is the nearest neighbor intermolecular interaction matrix element and a is the lattice spacing in the direction of the interactions. Using this energy relationship, the partition function z for the system can be written as

$$z = 1 + e^{-\Delta/kT} + \sum_{k=\pi/na}^{n\pi/na} 2e^{-[\Delta - 2\beta(1 - \cos ka)]/kT} \quad (1)$$

The zero of energy is taken at the energy of the trap. The trap depth Δ is the difference in energy between the trap energy and the energy of the $k = 0$ level of the exciton band. This is the depth which is measured spectroscopically since only the $k = 0$ level of the origin absorbs or emits light. The first term in z is the Boltzmann factor for the trap level, the second term is for the non-degenerate $k = 0$ level of the band. The summation is over the remainder of the exciton states which are doubly degenerate. The trap probability $P_{\text{trap}} = 1/z$, and therefore the intensity of trap emission $I_{\text{trap}} \propto 1/z$.

If a sample of known trap concentration is prepared and the trap depth Δ is measured spectroscopically, then β can be fit to the temperature dependence of the trap emission. As depicted in Fig. 1, two cases arise depending upon the sign of β . If β is negative the exciton band spans an energy range from Δ , the $k = 0$ energy, to $\Delta + 4\beta$, $k = \pm\pi/a$. If β is positive the band is inverted and it spans an energy range from Δ to $\Delta - 4\beta$. Thus the sign of β in addition to the magnitude of β determines the temperature dependence at the trap intensity. The above description gives excellent agreement with experiment for crystals of 1,2,4,5-tetrachlorobenzene which have one-dimensional excitons and traps of a single energy. In order for this description to work, the system must reach equilibrium within the 1 msec lifetimes of the excited states. This implies that excitations must

$$E(K) = E^0 + 2\beta \cos Ka$$

Fig. 1. Trap level and exciton band for systems containing regular and inverted exciton bands. (XBL 7210-5704)

be able to migrate to many trap sites in less than the lifetime. The traps in the 1,2,4,5-tetrachlorobenzene samples are of such low concentration that it is possible to distinguish between the two possible modes of exciton transport, coherent migration or random walk hopping. In the coherent model the velocity of an exciton is given by

$$V_g = \frac{1}{\hbar} \frac{\partial E(k)}{\partial k} \quad (2)$$

The average velocity at a temperature T is

$$\langle V_g \rangle = \frac{2\beta a}{\hbar} \frac{\sum_k \sin(ka) e^{-(2\beta \cos ka)/kT}}{\sum_k e^{-(2\beta \cos ka)/kT}} \quad (3)$$

At liquid helium temperatures $\langle V_g \rangle \approx 2700 \text{ cm}^2/\text{sec}$ for 1,2,4,5-tetrachlorobenzene which is more than adequate to insure equilibrium. In the hopping model, the median velocity is given by

$$V_{\text{hop}} = \frac{3}{g} \left(\frac{4\beta}{\hbar} \right)^{1/2} a \quad (4)$$

V_{hop} is found to be a factor of 10^6 smaller than $\langle V_g \rangle$ and is too small to allow the sample to come to equilibrium within the lifetime of

the states. Thus, coherent migration is established as the principal mode of exciton transport at liquid helium temperatures.

In addition to the above discussion, the model developed for the temperature dependence of trap emission also treats multidimensional exciton bands, systems in which there are traps of several different energies, the effect of spin lattice relaxation between the three triplet sublevels, and systems in which the excitons and traps have different lifetimes. The model applies equally well to fluorescent and phosphorescent traps.

5. PHOSPHORESCENCE MICROWAVE DOUBLE RESONANCE SPECTROSCOPY IN EXCITED TRIPLET STATES

William G. Breiland, Michael D. Fayer, Charles B. Harris, Allan M. Nishimura, Rodney M. Panos and Horst Schuch

The technique of optically detected magnetic resonance (ODMR) in phosphorescent triplet states in magnetic fields and zero field recently developed in these and other laboratories has provided experimentalists with a tool capable of elucidating many features of triplets that have been difficult to obtain via conventional optical spectroscopy or magnetic resonance techniques. Since phosphorescence from the lowest triplet state to the ground state singlet is generally specific from the individual magnetic spin sublevels, an analysis of the phosphorescence microwave double resonance (PMDR) spectra can yield spin-orbit symmetries of the individual spin sublevels and hence the orbital symmetry of the excited triplet state while a quantitative analysis of the changes in phosphorescence induced by microwave field or changes in the magnetization yield relative intersystem crossing rates and relative radiative rates associated with the sublevels. In addition to parameters associated directly with radiationless and radiative processes in the triplet state, ODMR provides a measure of the electron distribution in excited states from an analysis of the spin Hamiltonian which in zero field include the spin dipolar, the electron-nuclear hyperfine, and the nuclear quadrupole interactions.

These techniques were extended to a variety of aromatics.

a. 1,2,4,5-tetrabromobenzene

In 1,2,4,5-tetrabromobenzene the results showed that the phosphorescence originates from the undistorted $^3B_{1g}(\pi\pi^*)$ state. The sign and magnitude of the zero-field parameters were correlated to the spin dipolar interac-

tions in the $^3B_{1u}$ state and the large spin-orbit contributions to the zero-field splitting. Finally the excited triplet state values for the ^{79}Br and ^{81}Br nuclear quadrupole constants were obtained from an analysis of the zero field ODMR.

b. 1,4-dibromonaphthalene

Work was completed on 1,4-dibromonaphthalene (DBN) single and doped crystals at 1.4°K. The zero-field splitting parameters were measured for several trap emissions. The results of decay measurements by microwave-induced adiabatic inversion and conventional phosphorescence decay experiments were used to assign the symmetries of the triplet magnetic sublevels and also used to consider several phosphorescence mechanisms. Orbital symmetries of the triplet state of DBN were related to the zero field electron dipolar interactions and were used to consider the magnitude of the experimentally measured zero-field splitting. Finally, results of spin alignment measurements of several traps in DBN neat crystal were understood in terms of perturbation λ , phonon interaction.

c. 1,4-dichlorobenzene

Phosphorescence microwave double resonance (PMDR) spectra of p-dichlorobenzene have been obtained monitoring low temperature (~1.3°K) trap phosphorescence and used to make symmetry assignments of various vibronic bands present in the spectra. In addition, ratios of radiative rate constants of individual triplet spin sublevels to several vibrational states, the intrinsic lifetimes of all three triplet spin sublevels, and selective polarized phosphorescence from individual spin sublevels in various vibronic transitions have been measured. An analysis of these data along with explicit considerations of the p-chlorine perturbation on the aromatic ring elucidated the relationships between the orbital symmetries and the sign and magnitude of the zero-field electron spin dipolar interactions in the triplet state for the halobenzenes. On these bases an assignment of the orbital symmetry of the lowest excited triplet state of p-dichlorobenzene was established as $^3B_{1u}$.

d. Hexachlorobenzene

Preliminary PMDR data have shown that the excited triplet state in hexachlorobenzene doped in hexamethylbenzene exhibits many of the same features as 1,4-dichlorobenzene and the tetrahalogenated benzenes.

6. BREAKDOWN OF THE BORN-OPPENHEIMER APPROXIMATION IN RADIATIVE TRANSITIONS

Charles B. Harris, William G. Breiland and John C. Brock

Using phosphorescence microwave double resonance (PMDR) techniques, radiative contributions from the individual spin sublevels to various totally symmetric vibrations in the ground singlet manifold were determined for the lowest excited triplet state of 1,2,4,5 tetrachlorobenzene (TCB). Both h_2 -TCB and d_2 -TCB doped 1% m/m in durene were investigated and studies of naphthalene doped in TCB are in progress.

The TCB data demonstrated an explicit nuclear coordinate dependence of electronic matrix elements in the transition moment for phosphorescence to the ground state vibrational manifold. Theoretical expressions for the experimental observations developed within the framework of the Condon and Herzberg-Teller approximations fail to explain the results, implying that these approximations are not general enough to give a good description of radiative transitions in aromatic molecules. Additional terms in the Herzberg-Teller expansion and the breakdown of the Born-Oppenheimer approximation were shown to be alternatives which can be used to explain the experimental observations.

Further insight into the specific dependence of the electronic wave function on nuclear motion may be gained by analyzing the normal coordinate of the vibration in relationship to the positions of the nodal planes in the excited electronic state. The ratio might be relatively unaffected, for example, when the nuclear motion is associated with a direction that keeps the nuclei in a nodal plane of the electronic wave function. Examination of these relationships is presently under investigation.

7. COHERENT SPIN PHENOMENA IN MOLECULAR EXCITED STATES

Henry C. Brenner, William G. Breiland, Terence E. Gough, Charles B. Harris, Ronald L. Schlupp, and Horst Schuch

In phosphorescent triplet states, or, for that matter, in any state where the emission from the individual spin states is unresolved optically, it was shown earlier in these laboratories that modulation of the light at the Larmor frequency by an applied microwave field is unobservable unless the electric

dipole transition from the individual spin levels is of the same polarization. In many excited triplet states, however, the spin sublevels of molecules have different spin-orbit symmetries and thus direct detection of the Larmor term is usually forbidden.

In other words, unlike conventional magnetic resonance where components along x or y may be observed, optically detected magnetic resonance requires that the time-dependent density matrix describing the spin ensemble be displayed through the electric dipole transition moment. The result is that only components along z in the interaction representation are directly observable via a change in the rf-induced modulation of phosphorescence intensity. Since the coherence of the spin ensemble in the interaction representation is confined to the x-y plane, phasing or dephasing phenomena do not normally affect the phosphorescence polarization or intensity. Components of the spin in the x-y plane correspond simply to unchanging saturated populations of the two spin sublevels in the laboratory frame.

The ability to restore the ensemble from the x-y plane to the z axis is directly proportional to the extent of dephasing. If the spins are completely dephased in the x-y plane no further change along z can be brought about by an additional microwave perturbation and hence the population of the spin sublevels in the laboratory frame remains constant. On the other hand, if the ensemble can be in part restored from the x-y plane the spin sublevel populations in the laboratory frame will take on new values. The net result is that a further change in the phosphorescence intensity can be affected by additional microwave perturbations. It is expected therefore that many manifestations of spin coherence can be experimentally observed via optically detected magnetic resonance techniques. Furthermore the technique is capable in principle of measuring the ensemble coherence of as few as 10^4 excited state spins.

An apparatus has been constructed to allow the optical detection of electron spin echoes of excited states. In the construction of such apparatus, careful attention has been paid to the design of the microwave system to provide good impedance matching throughout. Impedance matching is important for both the efficient generation of high intensity microwave fields and to minimize unwanted reflection which distorts the pulse shapes. Currently clean 50 nsec pulses of any microwave phase having $H_1 = 4$ gauss are obtainable throughout the region 1.0 to 8.4 GHz.

Electron spin free precession in excited

states has been measured* point-by-point by observing the phosphorescence intensity after two $\pi/2$ microwave pulses, the first to prepare the coherent state and later a second to probe the instantaneous value of the coherence in the x-y plane by returning it to the z axis. Likewise, spin echoes in excited states have been optically detected by a three-pulse sequence $\pi/2, \pi,$ and $\pi/2$, the first two pulses being used to prepare the echo and the last pulse being used to monitor point-by-point the formation of the echo in the x-y plane by monitoring the effective population restored to z and the resulting change in the phosphorescence intensity at the end of a sequence.

Shallow traps in tetrachlorobenzene have been studied by these techniques, and a homogeneous T_2 of 4.1 μ sec observed over the temperature range $1.4 + 4.2^\circ\text{K}$ has been obtained. The value of 4.1 μ sec should be compared with the inhomogeneous T_2 of ~ 250 nsec. The echo decays are nonexponential, showing a beat frequency of approximately 0.9 MHz, indicating the presence of a splitting due to the unresolved ^{35}Cl hyperfine inter-echos matched by the inhomogeneous broadening in the conventional C. W. spectrum.

We have also successfully observed via optical detection rotary electron spin echoes and rotary echo trains in molecular excited triplet states utilizing a $\tau-2\tau'-2\tau-2\tau' \dots$ pulse train, where primed τ pulses are 180° phase shifted from unprimed τ pulses. Successful echoes have been observed for proto and deuterio 1,2,4,5-tetrachlorobenzene. This sequence is being used to examine the correlation function for energy migration in molecular crystals containing both traps and excitons. This is accomplished by varying τ . For very short τ then, diffusion ($\propto \tau^3$) can be neglected in the decay of the echo amplitudes while for long τ diffusion becomes proportionately more important.

Work has also begun on long-range guest-to-guest triplet energy transfer in mixed molecular crystals using optically detected magnetic resonance techniques at low temperatures. One potentially favorable system is phenazine and anthracene doped into diphenyl host crystals. It is known from published work in other laboratories that the phenazine triplet is populated almost exclusively through the top zero field level by selective inter-system crossing from the singlet manifold, and that the spin alignment is preserved upon transfer to anthracene, whose triplet lies several hundred wave numbers lower. The transfer proceeds either by direct exchange

* In collaboration with A. Pines.

transfer from phenazine triplet to anthracene ground triplet, or by means of diphenyl triplet excitons generated from singlet excited phenazine. Using this or another system where light emission is more intense, we are attempting to induce microwave transitions in the donor triplet and monitor the modulated phosphorescence of the acceptor triplet. This could answer the question of whether the transfer proceeds through the host triplet. Using the techniques for optical detection of triplet state spin echoes, recently developed in this laboratory, we are attempting to determine spin memory times upon energy transfer from donor to acceptor.

Finally, electron spin locking in molecular excited triplet states has been observed via optical detection. It is expected that virtually any process that affects spin lattice relaxation in the rotating frame will be amenable to study. This should allow the development of many new double resonance techniques involving other spins (electron and nuclear) and other processes such as acoustic phenomena.

8. COHERENT OPTICAL PHENOMENA IN MOLECULAR EXCITED STATES

Charles B. Harris, Allan M. Nishimura, and Robert M. Shelby

The coherence associated with an electric dipole transition of an ensemble of excited states can in principle be studied by using a sequence of light pulses similar to the microwave pulses developed for spin states in section 7. The importance of such studies in understanding radiative and radiationless relaxation phenomena from excited electronic states is that a direct measure of the ensemble phase can in principle be directly measured via its relationship to the total population left in an excited state after the application of a given light pulse sequence. The dephasing of the moment by various relaxation routes has been a topic of current interest in echo studies of electron spin states, but experimental work has been limited to slow processes in the analogous photon echo and relaxation phenomena due to previously unobtainable optical pulses shorter than several tens of nanoseconds. In an attempt to overcome these difficulties and study extremely fast processes (10^{-12} sec), we have constructed high power Nd:glass and ruby lasers, both of which have unusual stability and have been successfully mode-locked. In addition, single pulse selection has been obtained by using a spark-gap-triggered Pockels cell. We are presently in the

process of generating multiple-light-pulse trains of controlled amplitude. In addition to studying relaxation phenomena of states exhibiting an oscillating macroscopic electric dipole moment, the lasers are being used to study coherent times in exciton migration and to study energy trapping in defect and impurity sites in molecular crystals.

9. RESEARCH PLANS FOR CALENDAR YEAR 1973

Charles B. Harris

Our major emphasis will be to explicitly determine the nature of processes that destroy the coherent transport of electronic energy in molecular crystals. This will be approached from two types of experiments. The first will be to observe, as a function of temperature and applied magnetic field, the averaging effect of the exciton optically detected magnetic resonance resulting from exciton-phonon collisions. The EPR line-shape theory for coherent excitons developed in these laboratories is dependent upon the relative size of $(\omega_k^k - \omega_k^k')$ and $1/\tau_{kk}'$, where ω_k^k is an ESR transition frequency associated with a particular value of k and $1/\tau_{kk}'$ is the probability per unit time for scattering of an exciton in a state k to a state k' . In the coherence limit, $(\omega_k^k - \omega_k^k') > 1/\tau_{kk}'$ and the observed line is a superposition of individual ESR lines at different frequencies determined by the values of k . In the strong scattering, random walk case, $(\omega_k^k - \omega_k^k') \ll 1/\tau_{kk}'$, and a homogeneously narrowed line at the average value of k is expected.

In the coming months we intend to study phonon exciton scattering processes in applied magnetic fields. As mentioned above, the exciton spin Hamiltonian parameters are k dependent. Thus we expect that $\omega_k - \omega_{k'}$ will depend in general on the magnitude and direction of an applied magnetic field. Hopefully one can proceed smoothly from the coherent limit to the strong scattering limit by varying the field. One can then obtain information about the k dependence of $1/\tau_{kk}'$ and test out various models for phonon exciton scattering. The magnetic field studies will be complemented by experiments in which we vary the temperature, which affects the values of $1/\tau_{kk}'$ directly. Secondly, the observation of coherence times in excitons and the scattering processes will be probed by utilizing picosecond laser techniques.

Specifically, by optically exciting a crystal into an exciton state in a time on the order of 10^{-12} sec with a picosecond laser pulse, an ensemble of excitons are

produced in the $k = 0$ state of the crystal. If no exciton scattering occurs, one expects the time-dependent radiative decay from the exciton state to be a simple exponential to both electronic origin and a vibronic origin. If, however, the prepared $k = 0$ states scatter to other k states then the radiative emission to the electronic origin will not be the same as to the vibronic origin. In particular, the vibronic origin will not appear exponential until an equilibrium Boltzmann distribution is established in the exciton band (via phonon-exciton scattering), at which point the scattering into individual k states equals the scattering out of the k states. It is expected that the nonexponential behavior at early times reflects the scattering to nonzero k states with a rate proportional to the exciton density of states function times the phonon-exciton scattering interaction. The time dependence of exciton emission measured via fluorescence is expected to yield, therefore, the coherence time (the average lifetime of a k state) and thus a direct measure of the excitons mean free path in the crystal.

Finally, models for bimolecular exciton-exciton annihilation will be developed and tested in the coherent limit. Coherent exciton migration should allow two triplets to come close enough to each other to undergo triplet-triplet annihilation at a very accelerated rate. This results in the loss of the two triplets and the production of a ground state singlet and a highly excited singlet. The highly excited singlet can relax to the first excited singlet state and may then fluoresce. Fluorescence of this kind is known as delayed fluorescence. By studying the details of the coherent migration process and thereby determining as a function of temperature the probability of two triplets encountering each other, a model for the temperature dependence of delayed fluorescence can be developed from a statistical basis.

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Alexander Pines, Principal Investigator

1. NUCLEAR MAGNETIC DOUBLE-RESONANCE

Alexander Pines

Two perennial problems in the study of dilute nuclear spins in solids by nuclear magnetic resonance have been resolution and sensitivity. The observed spins may be dilute due to natural isotopic abundance or due to chemical dilution. The observation of these nuclei would open the way to many studies not previously accessible to conventional nuclear magnetic resonance. These include, for example, structural and dynamical features of impurities in solids, microscopic details of molecular motion in solids, phase transitions, spin relaxation phenomena, and quantum mechanical tunneling at low temperatures.

An approach to these problems has been made employing several well known features of solid state magnetic resonance. The problem of sensitivity is alleviated by transferring magnetic polarization from abundant surrounding nuclear spins (I) to the dilute nuclear spins (S) under observation. In a typically useful example the dilute spins could be $S \equiv {}^{13}\text{C}$ and the abundant spins $I \equiv {}^1\text{H}$. The polarization transfer can be accomplished in many ways, only one or two of which (consisting of transfer in the I, S double rotating frame) have been studied to date. In this way, the detected power signal/noise can be enhanced by a factor of $G \approx (\gamma_I/\gamma_S)^2 N_I/N_S$ over conventional Fourier transform spectroscopy. (γ is the magnetogyric ratio and N the number of spins.) For ${}^1\text{H} - {}^{13}\text{C}$ $G \approx 10^3$ and for ${}^1\text{H} - {}^{15}\text{N}$, another important case, $G \approx 10^5$.

The problem of resolution is overcome by employing a solid state version of spin decoupling demonstrated by Searles and Cotts, and by Mehring, Pines, Rhim, and Waugh. This involves intense irradiation of I spins by continuous or multiple-pulse rf fields. In this way, the resolution has been improved for ${}^{13}\text{C}$ from ~ 5 kHz to ~ 15 Hz. The technique combining the sensitivity and resolution enhancement has been termed "proton-enhanced nuclear induction spectroscopy."

The sensitivity gain has been verified in a number of preliminary cases. For example, a high resolution spectrum of ${}^{13}\text{C}$ in ~ 50 mg of solid adamantane was obtained in ~ 0.8 sec with good signal/noise. Spectra have been obtained in this way for ${}^{13}\text{C}$, ${}^{15}\text{N}$, and ${}^{29}\text{Si}$ in a large number of solid materials at

various temperatures. Examples are shown in Figs. 1 and 2. Chemical shielding anisotropies, which are difficult to obtain by any other means, have been reported for most of these cases. When available, previous theories of chemical shielding, such as those of Karplus and co-workers, fail to agree with experimental results. Recent machine calculations of Ditchfield are more successful for ${}^{13}\text{C}$.

The measurements provide much more complete information than is available from liquid crystal experiments. In particular, by using single crystals, complete information on ${}^{13}\text{C}$ shielding tensors has been obtained in a number of compounds including durene, glycine, and oxalates. The direction of the principal axis of the shielding tensor in the molecule and the magnitudes of the principal values are extremely sensitive to structure and bonding and should prove valuable aids in the study of electronic structure in solids.

In addition to these structural studies, several dynamical studies have been made. These include high resolution examination of I-S cross-relaxation and studies of molecular

Fig. 1. Proton-enhanced NMR spectrum of natural abundance ${}^{13}\text{C}$ in polycrystalline acetic acid. The low field resonance is from the carbonyl carbon and the high field one from the methyl group. The spectra display characteristic shapes for anisotropy of the chemical shielding tensors. Principal values of the tensors can be read directly from the sharp edges of the powder peaks. The horizontal axis is in ppm relative to an external reference of benzene.

(XBL 731-5627)

Fig. 2. ^{13}C NMR spectrum in a single crystal of durene obtained by proton-enhanced nuclear induction spectroscopy. Ten lines are observed in this orientation of the crystal reflecting the ten magnetically inequivalent carbons of the two molecules in the unit cell. In the liquid, only three lines are observed. The most shielded component of the aromatic shielding tensor is perpendicular to the ring. The horizontal scale is in ppm relative to an external reference of benzene. (XBL 731-2021)

motion. The complete dependence of cross-relaxation on rotating field strengths and frequencies is important for comparison with density matrix perturbation theories of relaxation. The measurements yield details on fluctuation spectra of the cross-coupling between nuclear spins. In the ^{19}F - ^{43}Ca double-resonance in CaF_2 studied by Hahn and co-workers, the spectrum was found to be an exponential function of the rotating frame Zeeman splitting, implying a Lorentzian correlation function for the cross-coupling fluctuation. This is different from the Gaussian form normally assumed for these functions. We have carried out preliminary experiments which suggest that this behavior is quite general, but a substantial amount of work remains to be done in this area both on theory and on experiments.

Molecular motion can be studied by observing both high resolution spectral changes and spin-relaxation times (cross-relaxation and spin-lattice relaxation). Again, only preliminary work has been done

and this remains one of the most exciting aspects of these new techniques. Spectral changes have confirmed that in benzene and hexamethylbenzene, motion is facile about the molecular hexad axis as is known from wide-line studies and neutron diffraction. Activation energies have been measured and are in agreement with accepted values. In adamantane, and in camphor, two "roundish" molecules, we have found that rotational motion is more or less isotropic in the solid, as may be expected. Rotational correlation times are $\sim 10^{-9}$ sec at room temperature, suggesting rather serious intermolecular forces in the crystals.

2. NUCLEAR SPIN THERMODYNAMICS AND MULTIPLE-PULSE NUCLEAR MAGNETIC RESONANCE

Alexander Pines

In rigid solids, where nuclear spins are strongly coupled together by dipolar interactions and only weakly coupled to the lattice, the spin system may be regarded for many purposes as isolated and the concepts of thermodynamics and statistical mechanics applied. The spin temperature hypothesis states that after a spin-spin relaxation time T_2 , the system reaches internal equilibrium and is described by a density matrix $\rho_{\text{eq}} = (1/2) \exp(-\beta H)$ appropriate to a canonical ensemble. Many important phenomena have been understood and many elegant experiments have been devised on the basis of this theory. Two aspects of this have been looked at by us and studies will continue.

In the first place, we may ask what happens when the Hamiltonian H becomes time dependent due, say, to phase and amplitude modulated rf irradiation? In this case nuclear spin thermodynamics no longer applies in the laboratory frame. We have shown, however, that in a well-chosen "toggling" frame of reference the Hamiltonian may be effectively time independent and thermodynamics applied. The thermodynamical quantities of interest such as heat capacity and entropy are obtained from the density matrix employing the calculated effective or average Hamiltonian. The latter is calculated using coherent averaging theory. This approach is a direct extension of the Redfield ideas of spin temperature in the rotating frame. This phenomenon is extremely valuable since it allows a modification of thermodynamical parameters by carefully monitored external perturbations. This should find applications to double-resonance and to polarization enhancement in production of nuclear ferro- and antiferromagnetism. Preliminary experiments have been performed

on the ^{19}F spins in a crystal of CaF_2 . Under a train of intense phase-alternated rf pulses applied at resonance the system was found to reach a state of internal equilibrium, and the subsequent increase in spin temperature as a function of nutation angle agreed well with theory.

Secondly, it has been shown that the spin-temperature hypothesis must be employed with caution. If the sign of the Hamiltonian describing interactions between spins could be reversed, then the random phase approximation which forms the basis for the selection of a canonical density matrix is no longer applicable, and coherent phenomena could be observed which would appear to violate the expectations of spin thermodynamics. Such an effective time-reversal has indeed been produced by Rhim, Pines, and Waugh in ^{19}F and ^1H spins in several solids, and spin echoes following a free induction decay have been observed. The time-reversal is effected by carefully selected multiple-pulse rf irradiation. An example on the ^{19}F spins of CaF_2 is shown in Fig. 1. The free induction decay in a solid had previously been thought by some workers to be an irreversible process. The phenomenon has important application to the study of line shapes, high resolution nuclear magnetic resonance in solids, and spin diffusion.

The theory of the response of coupled nuclear spins to such irradiation must be well understood in order that these phenomena be exploited efficiently. The theory was extended by Pines and Waugh to cover the general case of irradiation far from resonance. It

Fig. 1. Time reversal of ^{19}F free induction decay in CaF_2 . Following a 90° pulse we observe the decay, following which a strong rf perturbation is applied at the ^{19}F resonance frequency. This effectively reverses the sign of the nuclear spin dipolar coupling and produces a spin echo when the spins are again allowed to propagate freely. The echo maximum is $\sim 500\mu$ sec from the initial 90° pulse.
(XBB 731-278)

was shown that whatever the irradiation, the average Hamiltonian for dipolar interactions is just a (Van Vleck) truncated dipolar Hamiltonian along some axis in the rotating frame. Recipes for calculating the relevant parameters were given. It was shown that this should also be extremely useful for applications to line-narrowing, time-reversal, and nuclear double-resonance in solids.

3. RESEARCH PLANS FOR CALENDAR YEAR 1973

Alexander Pines

a. High Resolution Nuclear Magnetic Resonance in Solids

Work will continue on techniques to enhance both resolution and sensitivity. We plan specifically to develop ultra-high sensitivity by employing indirect detection of S spins by monitoring destruction of I polarization in cross-relaxation. The dynamics of polarization transfer will be studied and alternative transfer methods devised. We plan to investigate multiple adiabatic cross-over as a method for producing efficient total transfer of I to S polarization. The experiments will involve a large amount of technical work, and a versatile low temperature spectrometer is being constructed. This will operate with an on-line minicomputer and superconducting solenoid, and will have facilities for operation with multiple frequencies, high power, and flexible timing in phase and amplitude modulation. The techniques will be used to extract information on structure and motion in organic and "fluxional" organometallic compounds.

In addition techniques will be developed to enhance sensitivity by strengthening the spin lattice coupling. This will be done by chemical doping and by optical pumping. Limitations posed by spin diffusion will be examined.

b. Ferroelectric Phase Transitions

Studies will be undertaken to obtain microscopic details on phase transitions in ferroelectric crystals of the KDP (potassium dihydrogen phosphate) class. We hope to observe details of the transition in spectral changes of the high resolution spectrum of ^1H , ^{31}P , ^{13}C , etc. This should supplement information obtained from nuclear quadrupole resonance studies of ^2H and ^{75}As and help to clarify the role of hydrogen-bonding on the ferroelectric behavior in these compounds. We plan to extend these studies later to look at hydrogen bonding in solids exhibiting optical activity.

c. Optical-Nuclear Double-Resonance

Excited triplet states of organic molecules in solids have been studied by Harris and co-workers by phosphorescence-microwave double-resonance. Electron spin echoes have been produced and are thought to decay due to modulation of nuclear-electron hyperfine interactions by nuclear spin diffusion. Two types of nuclear magnetic resonance experiments will be undertaken:

- (i) To observe the nuclei near the excited triplet molecule. This should yield information on the local structure and information on resonance frequencies which is important for understanding the electron spin relaxation.
- (ii) To develop methods to inhibit spin diffusion effectively. This should be useful later in extracting homogeneous electron spin line widths.

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LBL report

1. W. G. Breiland, C. B. Harris and A. Pines, Optically Detected Electron Spin Echoes and Free Precession in Molecular Excited States, LBL-1412, December 1972 (submitted to *Phys. Rev. Letters*).

Papers presented

- *1. Proton-Enhanced Nuclear Induction Spectroscopy. Chemical Shielding and Nuclear Spin Relaxation of ^{13}C in Solids, Thirteenth Experimental NMR Conference, Asilomar, California, 1972.
- *2. Proton-Enhanced NMR of Dilute Spins in Solids, Colloque Ampere, Turku, Finland, 1972.
- *3. High Resolution Nuclear Magnetic Resonance in Organic Solids, Meeting of the NMR Discussion Group of the Chemical Society (London), Surrey University, England, 1972.

* Not supported by IMRD (work done before joining IMRD).

Ronald R. Herm, Principal Investigator

1. COLLISION DYNAMICS OF "ALKALI-LIKE" ATOMS

Boyd L. Earl, Lara A. Gundel, Ronald R. Herm, Shen-Maw Lin, Lambert C.-H. Loh, Charles A. Mims, and Charlotte M. Sholeen

Our past research efforts have concentrated on experimental studies of the collision dynamics of gaseous atomic species with relatively low ionization potentials. Research during 1972 which was directed along these lines included: (1) measurements of the cross sections for collisional quenching of excited alkali atoms produced by photo-dissociation of alkali halide vapor (BLE); (2) a study of the electronic chemiluminescence from HgCl which is produced in a flowing Hg-Cl₂ vapor mixture upon irradiation by the 2537 Å Hg resonance line (LAG); (3) crossed beam studies of the reactions of Li atoms with halogen-containing molecules (CMS and LAG); (4) crossed beam studies of the collisional quenching of Hg (6s6p³P_{0,2}) (LC-HL); and (5) crossed beam studies of some reactions of Ba, Sr, Ca, and Mg atoms (S-M and CAM). Since our 1972 efforts were an extension of earlier studies described in previous DMRD Annual Reports, most of this work will not be described in this present report. However, it seems worthwhile to include the following description of our results for some of the alkali-earth atom reactions because this work is mentioned only briefly in the 1971 Annual Report.

Ba, Sr, Ca, and Mg + ICl and Ba + BrCN*-- Primitive product angular distributions of MCl and MI from Ba, Sr, Ca, and Mg + ICl and of BaCN and BaBr from Ba + BrCN have been measured in a crossed-beam apparatus employing an electron bombardment ionizer-mass filter detector. Product center-of-mass (CM) recoil angle and energy distributions have been fit to the measured laboratory (LAB) angular distributions by averaging the CM + LAB transformations over the (non-thermal) beam speed distributions. Both the MCl and MI CM product distributions from M + ICl are relatively insensitive to the identity of the attacking atom, except that practically no MgI is formed in the Mg reaction. Other product yield ratios are estimated as ~ 2:1 for MCl:MI from ICl, ~ 10:1 for BaCN:BaBr from BrCN. All of the reactions favor forward CM product scattering (i.e., MX scattered within 90° of the direction defined by the incident M), although the preference is especially weak in the Ba + BrCN → BaBr + CN reaction. For the ICl reactions, MI are

formed with broader CM cross sections and higher average product recoil energies, E', than are MCl; average E' values are ~ 8-12 kcal/mol for MI + Cl and ~ 3-5 kcal/mol for MCl + I.

Ba, Sr, and Ca + Some Halides of Methane-- This same apparatus has also been used to measure angular distributions of the following mass filter detector signals: MI⁺ from Ba, Sr, and Ca + CH₃I and CH₂I₂; BaI⁺ from CF₃I; and BaCl⁺ from Ba + CCl₄. The results show that the MI + CH₃ products from M + CH₃I scatter predominantly backwards in the CM system with substantial recoil energy (average E' value ~ 10-15 kcal/mol); these results are very similar to those observed for the analogous alkali atom reactions. All of the other reactions preferentially scatter products into the forward CM hemisphere. For these reactions, the MX⁺ mass filter signal might arise from ionization of a mono- or di-halide product. However, both the CH₂I₂ and CF₃I reactions show striking differences from those of the analogous alkali reactions: for Ba + CF₃I, a weak BaI⁺ mass filter signal is also observed; and the MI⁺ LAB angular distributions from Ba, Sr, and Ca + CH₂I₂ are only slightly broader than the calculated angular distributions for the center-of-mass velocity vector. These differences are quite reasonable if one assumes that MI₂ (and possibly MI as well) forms in the CH₂I₂ reactions and that BaI⁺ (and probably BaI as well) is formed from Ba + CF₃I.

* Abstracted from LBL-1134.

2. CROSSED BEAM REACTIONS OF BaF₂ WITH BC1₃

Richard Behrens, Jr., Andrew Freedman, Timothy P. Parr, and Ronald R. Herm

The development of the electron bombardment ionizer-mass filter "universal" detector makes possible crossed beam studies of the reaction dynamics of a variety of high temperature species. Thus, we have recently examined the reactive scattering from crossed beams of BaF₂ (at 1550°K) and BC1₃ (at 340°K). We have observed BFCl⁺ and BF₂⁺ mass filter signals of reactively scattered species. (A BaCl⁺ reactive scattering signal cannot be distinguished from a BaF₂⁺ non-reactive signal.) The BF₂⁺ signal must be due to the reaction:

The BFCl^+ signal might arise from BF_2Cl from reaction (1) or from BFCl_2 from:

We have not observed signals due to BaFCl^+ , BaCl_2^+ , BF_2Cl^+ , or BFCl_2^+ ; however, this is not surprising, as the product molecules would be expected to fragment upon electron bombardment ionization.

Results are still preliminary and center-of-mass product distributions have not been obtained because of an undetermined "viewing factor" distortion in the measured laboratory angular distribution. However, we would emphasize that our beam intensities are sufficiently low to ensure "single collision" conditions. Furthermore, we estimate that our apparatus sensitivity is such that the observed BF_2^+ signal implies a total reaction cross section, Q_R , of at least $1 \text{ \AA}^2$ for reaction (1). This study was originally undertaken because it was anticipated that $Q_R \geq 1 \text{ \AA}^2$ for reaction (2) because of the likely stability of the intermediate collision complex. In analogy with the alkali halide-boron trihalide adducts, this complex was expected to have an $(\text{BaF})^+(\text{BCl}_3\text{F})^-$ structure and to dissociate into the products of reaction (2). The occurrence of reaction (1) was surprising and might be due to a "secondary complex" formed as BaFCl and BCl_2F attempt to separate; the dipole-dipole attraction between these products might favor such snarled secondary encounter trajectories.

3. RESEARCH PLANS FOR CALENDAR YEAR 1973

Ronald R. Herm

Crossed beam studies of the reaction dynamics of Li and Na atoms will continue through 1973 into 1974. Our other studies grouped under the heading of "alkali-like" atoms in this report should be completed during 1973. During 1973, we also expect to complete the final assembly of our more sophisticated "universal detector" crossed beam apparatus, which was described in the 1971 Report.

We will seek out new themes for our crossed beam studies of collision dynamics during 1973. One of these will be studies of the reaction dynamics of high temperature species. This will continue to include some studies of reactions of metal atoms. Thus, a few reactions of alkaline-earth atoms will be examined in finer detail; reactions of Group III A atoms (notably Al) will also be studied. Further examples of bimolecular

molecule-molecule reactions, such as the $\text{BaF}_2 + \text{BCl}_3$ reaction described in the previous section, will also be sought. However, most of our efforts will be directed towards the study of reactions of molecular free radicals; initially, the reactions of the OH radical will be studied. These studies are likely to be difficult because of problems in the generation of an intense radical beam. However, for certain radicals, such as OH, it should be possible to overcome this difficulty by operating the beam source at sufficiently high temperatures so that the free radical becomes a major, or dominant, equilibrium species. Another theme which will be explored envisions the use of the phenomenon of condensation in expansion from a high pressure source as a method of preparation of unusual molecules for collision dynamics studies. Possibilities here include the study of reactions of weakly bound "van der Waals" molecules (e.g., Ar_2). Our progress in these areas during 1973 will be dependent on available funds, so that we may seek outside support as well.

4. 1972 PUBLICATIONS AND REPORTS

Ronald R. Herm and Associates

Journals

1. Boyd L. Earl, Ronald R. Herm, Shen-Maw Lin, and Charles A. Mims, Photodissociation of NaI Vapor and the Energy Dependence of the Quenching of $\text{Na}^*(3p^2P)$ by Foreign Gases, *J. Chem. Phys.* **56**, 867 (1972) (LBL-102).
2. Charles A. Mims, Shen-Maw Lin, and Ronald R. Herm, Crossed Beam Collision Mechanics: Reactions of Ca, Sr, and Ba with HI and Limits on D_0^0 for CaI, SrI, and BaI, *J. Chem. Phys.* **57**, 3099 (1972) (LBL-489).

LBL reports

1. Shen-Maw Lin, Molecular Beam Kinetics (Ph.D. thesis), LBL-891, September, 1972.
2. Shen-Maw Lin, Charles A. Mims, and Ronald R. Herm, Crossed Beams Chemistry: Reactions of Ba, Sr, Ca, and Mg with Cl_2 and Br_2 , LBL-1126, August, 1972 (submitted to *J. Chem. Phys.*).
3. Charles A. Mims, Shen-Maw Lin, and Ronald R. Herm, Crossed Beam Product Angular Distributions: MCl and MI from Ba, Sr, Ca, and Mg + ICl and BaCN and BaBr from $\text{Ba} + \text{BrCN}$, LBL-1134, October, 1972 (submitted to *J. Chem. Phys.*).

5. Shen-Maw Lin, Charles A. Mims, and
Ronald R. Herm, Crossed Beams Reactions of
Ba, Sr, and Ca with Some Halides of Methane,
LBL-1175, December 1972. (submitted to
J. Phys. Chem.)

Harold S. Johnston, Principal Investigator

Introduction. In previous years we have developed a new method for observing the spectra and chemical kinetics of reactive intermediates (for example, free radicals) produced photochemically by relatively low intensity light sources. Within the last two years it has become apparent that this work is pertinent to use of the stratosphere by supersonic transports. In 1972 our regular program was substantially expanded by a contract from the Department of Transportation. Our contract is one of 50 in the country supported by the Climatic Impact Assessment Program of the Department of Transportation. The overall goal of the national program is to assess the properties, resources, and limitations of the stratosphere as a region for transportation. Our project concerns the spectra and photochemistry of the oxides of nitrogen, free radicals based on water (H, HO, HOO), and ozone.

Fig. 1. Graph showing the room temperature spectrum of nitric acid vapor. XBL 726-6417)

1. EXPERIMENTAL STUDIES

a. Visible and Ultraviolet Absorption Spectra of Oxides of Nitrogen and Oxy-Acids of Nitrogen

Richard Graham and Harold S. Johnston

The goal is to obtain accurate, quantitative absorption spectra at temperatures and pressures close to stratospheric conditions (1 to 100 Torr, 200-300°K) for the following gases: NO₂, NO₃, N₂O₃, N₂O₄, N₂O₅; HNO₃, HNO₂; O₂, O₃. The room temperature spectrum of nitric acid vapor is given as Fig. 1. The room temperature spectra of NO₂, NO₃, N₂O₅, and HNO₂ have been obtained, but the work is not yet complete. A major effort has been devoted to converting the long path (32 meter, ultraviolet; 50 meter, infrared) spectrometers for use at low temperatures. The converted instruments are to be used for kinetic studies and for photochemical reactions as well as for spectroscopic measurements.

b. Quantum Yields for the Photolysis of Nitric Acid Vapor

Ted Chang and Harold S. Johnston

In the stratosphere, nitric acid is formed from hydroxyl radicals and nitrogen dioxide:

Nitric acid is destroyed by hydroxyl radicals:

and by photolysis by ultraviolet radiation:

The steady-state ratio of nitrogen dioxide to nitric acid is

$$\frac{[\text{NO}_2]}{[\text{HNO}_3]}_{\text{ss}} = \frac{k_2}{k_1} + \frac{k_3}{k_2[\text{HO}]} \quad .$$

The rate constants of reactions (1) and (2) are known, and the rate of photolysis of nitric acid is needed.

The photolysis of nitric acid vapor is a very complex laboratory reaction. Nitrogen dioxide is photolyzed by the same radiation that photolyzes nitric acid vapor. The product, NO, undergoes surface-catalyzed reaction with nitric acid. We are studying this photochemical reaction with a variety of experimental methods. The goal is to identify the primary photolysis products and the quantum yield as a function of wavelength. Results obtained at 210 nm and at 290 nm indicate a primary quantum yield of about 1,

and the primary product is probably HO (it must be either H or HO to account for observed products).

c. The Rate of Reaction of Nitrogen Dioxide with Ozone

T. T. Paukert, John Birks, and Harold S. Johnston

The fastest catalytic cycle for ozone destruction by the oxides of nitrogen under stratospheric conditions is the NO₂ cycle:

There is another cycle that may be very important below 22 km:

The key reaction in the NO₃ cycle is that between NO₂ and ozone. This reaction has been observed only at room temperature and over a very narrow temperature range. The temperature range is entirely too narrow to support an extrapolation to stratospheric temperatures. This reaction is being studied in a cell with 3 meter optical path and with temperature controls down to 230°K. Results are being obtained, but the study is not yet complete.

d. The Photolysis of Nitrogen Dioxide

Alan B. Harker and Harold S. Johnston

Although the photolysis of nitrogen dioxide has been studied by many different investigators, there has remained some disagreement on important aspects of the study. Also the transient appearance and decay of nitrogen pentoxide is of some interest. A study of this reaction has been completed and an article submitted for publication. Our results are in good agreement with one group of literature values, but disagree with the results of one investigator.

e. The Free Radicals ClO₂

Alan B. Harker and Harold S. Johnston

When chlorine atoms are produced in the

presence of oxygen, the "odd chlorine" is in the forms: Cl, ClO, ClOO (peroxy form). We have studied the kinetics of the ClOO and ClO radicals, the ultraviolet spectra of ClO and ClOO, and the infrared spectra of ClOO. The addition of carbon monoxide to this system leads to additional ClO:

In an effort to obtain the infrared spectrum of ClO, we added carbon monoxide. The infrared spectrum of ClO was probably detected, but it is partly obscured by a strong radical spectrum, perhaps ClOOO or OO(OO)Cl. This study has been completed and is being written up for publication.

f. The Quantum Yield of Singlet Oxygen from Oxygen Photolysis

Douglas R. Martin and Harold S. Johnston

When ozone absorbs radiation throughout the visible and ultraviolet region, the primary photochemical reaction is:

However, the electronic state of the oxygen atom product varies with wavelength: below 290 nm it is O(¹D), above 320 nm it is O(³P), but between 290 and 320 nm the quantum yield for O(¹D) drops from one to zero. The rate of formation of O(¹D) in the troposphere and lower stratosphere is very sensitive to how the quantum yield for formation of O(¹D) varies with wavelength.

We have under way a study of the yield of O(¹D) as a function of wavelength for narrow (1 nm) bands between 290 and 330 nm.

g. Fluorescence of Sulfur Dioxide

Douglas R. Martin and Harold S. Johnston

The dynamics of vibrational energy transfer in highly excited molecules can, in favorable cases, be studied by means of fluorescence studies. We have studied the fluorescence of SO₂ in a large (22 liter) spherical Pyrex bulb equipped with silica windows. The wavelength distribution of fluorescence radiation as a function of pressure (around 1 micron) has been followed for various narrow bands of exciting radiation. This study has been completed, and the preparation of a thesis and journal article is in progress.

h. Reactivity of Hydroxyl Radicals as a Function of Vibrational Energy State

Jere E. Streit and Harold S. Johnston

Hydroxyl radicals, HO, are produced in a large, low-pressure apparatus from the reaction of hydrogen atoms and nitrogen dioxide:

The hydroxyl radicals are produced in excited vibrational states, which are observed by means of emissions spectra. The rate of reaction of vibrationally excited HO radicals with ozone is being followed.

2. THEORETICAL STUDIES

a. Instantaneous Global Rates of Formation and Destruction of Ozone in the Stratosphere

Gary Z. Whitten and Harold S. Johnston

For more than 10 years atmospheric scientists have recognized that ozone is produced from sunlight much faster than it is destroyed by reactions involving pure oxygen and nitrogen. "Something else" is very active in destroying ozone in the natural stratosphere. The role of air motions in the stratosphere make very difficult the evaluation of the magnitude of the role of "something else." We have devised a relatively simple computational procedure that gives the following balance sheet for the global natural stratosphere for rates per second (any second) in units of 10^{29} molecules of ozone:

Ozone formation	+500
Loss in "pure air"	-86
Transport to troposphere	-6
"Something else"	-408

Thus the mysterious "something else" accounts for over 80% of the natural removal of ozone. We find 4×10^9 molecules NO_x (NO and NO_2) per cm^3 in the stratosphere to be sufficient to account for the needed 408 units of ozone loss. However, some of this loss is probably brought about by water vapor, especially in the upper half of the stratosphere.

b. Statistical Studies of "Ozone Data for the World, 1960-70"

Gary Z. Whitten and Harold S. Johnston

A large network of stations has regularly reported daily and monthly measurements of

total ozone since 1960. For a small number of these stations (10 out of about 90), Komhyr, Barrett, Slocum, and Weickmann [Nature 232, 390 (1971)] found that over the 10 year period 1961-70 (inclusive) ozone appeared to increase by 2 to 10%. In the spring of 1972 we started a statistical study of all the data, using the procedure of Komhyr et al., with some improvements in certain details. We expected to find as many stations showing decreases as Komhyr found with increases, and we expected the global average change to be zero within experimental error. To our surprise we confirmed the previous study and found an average increase of ozone of 4.5 ± 1.2 (2 σ) percent per decade (1960-70) for all stations. The increase was larger for the period 1963-70. For the period 1963-70 the increase was $4.6 \pm 1.4\%$ for all stations; it was $5.6 \pm 1.5\%$ in the northern hemisphere and $7.6 \pm 3.2\%$ for stations north of $50^\circ N$. On the other hand, ozone decreased during the three years 1960-62 at a percentage rate per decade of: -7.1 ± 6.5 (2 σ) for all stations, -7.6 ± 7.0 for northern hemisphere, and -12.6 ± 10.6 above $50^\circ N$.

These changes as a function of space and time are consistent with a hypothesis that the decreases (1960-62) were due to nitric oxide injected into the stratosphere by nuclear bomb tests (1952-62), and that the increase of ozone (1963-70) was the world slowly returning to normal after the cessation of nuclear tests in 1962.

c. Activation Energies for the Dissociation of Diatomic Molecules

John Birks and Harold S. Johnston

An analysis of all data on the dissociation of diatomic molecules showed that the observed decrease of activation energy (no values well below the dissociation energy) with increasing temperature can be explained in terms of non-equilibrium distributions over vibration levels of the molecule and in terms of allowed direct decomposition from any and all vibrational states.

3. RESEARCH PLANS FOR CALENDAR YEAR 1973

Harold S. Johnston

During calendar 1973, we plan to study the absorption spectra of several oxides of oxacids of nitrogen at temperatures comparable to the stratosphere, to study quantum yields (HNO_3 , O_3 , NO_3) as a function of wavelength, to study the rate of reaction of NO_2 with ozone, and to study several photochemical

reactions involving free radicals based on water (H , HO , HOO). The theoretical studies will focus on further identification of the important reactions in the stratosphere. As others determine the actual distribution of NO_x in the stratosphere, we are prepared to calculate whether or not this amount of NO_2 is sufficient to be the "something else" that now removes 80% of the naturally produced ozone.

4. 1972 PUBLICATIONS AND REPORTS

Harold S. Johnston and Associates

Journals and book

1. H. S. Johnston, The Effect of Supersonic Transport Planes on the Stratospheric Ozone Shield, *Environmental Affairs* 1, 735 (1972).
2. T. T. Paukert and H. S. Johnston, Spectra and Kinetics of the Hydroperoxyl Free Radical in the Gas Phase, *J. Chem. Phys.* 56, 2824 (1972) (UCRL-19109 Rev.).
3. H. S. Johnston, The Concorde, Oxides of Nitrogen, and Stratospheric Ozone, *Search* 4, 276 (1972).
4. H. S. Johnston, Newly Recognized Vital Nitrogen Cycle (Oxides of Nitrogen/Stratospheric Photochemistry/Ozone Balance), *Proc. Nat. Acad. Sci.* 69, 2369 (1972).
5. C.-H. Wu and H. S. Johnston, Molecular Modulation Mass Spectrometry Kinetic Study of the ClO Free Radical, *Bull. Soc. Chim. Belges* 81, 135 (1972).
6. J. Birks and H. S. Johnston, Activation Energies for the Dissociation of Diatomic Molecules Calculated from Molecular Properties, *Acc. Chem. Res.* 5, 327 (1972) (UCRL-20514 Rev.).

7. H. S. Johnston, in *The Oxides of Nitrogen and Photochemical Smog, Atmospheric Chemistry and Air Pollution* (Air Resources Center, Oregon State University, 1972) p. 69.

Papers presented

1. H. S. Johnston and Gary Whitten, Instantaneous Photochemical Rates in the Global Stratosphere, presented at the International Ozone Symposium, Arosa, Switzerland, August 21-25, 1972 (LBL-1178).
2. H. S. Johnston and Gary Whitten, Sensitivity Tests for Sufficiency of the Chapman Reactions, presented at the Meeting of American Geophysical Union, San Francisco, December 5, 1972.
3. H. S. Johnston, Laboratory Chemical Kinetics as an Atmospheric Science, Presented at Survey Conference on Climatic Impact Assessment Program, U.S. Department of Transportation, Cambridge, Mass., Feb. 15-16, 1972. (LBL-497.)

LBL reports

1. A. B. Harker, Reaction Kinetics of the Photolysis of NO_2 , and the Spectra and Reaction Kinetics of the Free Radicals in the Photolysis of the Cl_2-O_2-CO System (Ph.D. thesis), LBL-1114, September 1972.
2. Harold Johnston and Richard Graham, Gas Phase Ultraviolet Absorption Spectrum of Nitric Acid Vapor, LBL-1179, October 1972.
3. Harold Johnston and Gary Whitten, Instantaneous Photochemical Rates in the Global Stratosphere, LBL-1178, October 1972.

Bruce H. Mahan, Principal Investigator

1. RECOMBINATION OF GASEOUS IONS*

Bruce H. Mahan

The mutual neutralization of gaseous ions is one of the important mechanisms by which an ionized gas can decay to neutrals. The process can occur by parallel bimolecular (two ion) or termolecular (two ions, one neutral) reactions, and the relative importance of these mechanisms depends on the total gas pressure. At pressures above one atmosphere and at room temperature, the rate of recombination by either mechanism is limited by the rate at which ions diffuse toward each other.

We have reviewed the experimental and theoretical work on gaseous ion recombination, much of which was done in our laboratory. The general reliability of the data has been assessed, and comparisons made with various theories. The rate coefficients for both bimolecular and termolecular processes can in fact be calculated from the properties of the reactants and possible products to within an order of magnitude, which is a uniquely satisfactory situation in chemical kinetics. Nevertheless, discrepancies between theory and experiment suggest several ideas and experiments which should be pursued.

*Abstracted from a manuscript to be published in *Advances in Chemical Physics*, 1973.

2. THE $O_2^+ - C_2D_2$ REACTION: AN ENDOERGIC STRIPPING PROCESS*

Ming Hwa Chiang, Bruce H. Mahan, and Charles Maltz

We have determined the product DO_2^+ velocity vector distributions for the endoergic atom abstraction reaction

at a number of values of the initial relative energy. Two examples of these distributions are shown in Fig. 1. From these product velocity vector maps, it is clear that the abstraction reaction takes place by a spectator stripping mechanism in which little or no momentum is transferred to the C_2D fragment. This type of mechanism had heretofore

Fig. 1. Contour maps of the specific intensity of O_2D^+ from the $O_2^+ - C_2D_2$ reaction at 125 and 99.4 eV laboratory energy. The small crosses locate the velocity of O_2D^+ formed by the spectator stripping process. The circles marked $Q = -2.3$ eV and $Q = -10$ eV are, respectively, the velocity limits for products with the minimum and maximum allowable internal excitation consistent with their stability in the ground electronic state. The angles are measured in the barycentric system. (XBL 721-5967)

fore been associated with exoergic processes exclusively, and the experiments reported here demonstrate that spectator stripping can occur for endoergic reactions as well.

An energy threshold for the abstraction occurred at a laboratory energy of approximately 40 eV for the O_2^+ projectile. At this laboratory energy, O_2^+ has an energy relative to the entire C_2D_2 molecule of 17.7 eV, much in excess of the endoergic of 2.23 eV. However, the energy of O_2^+ relative to the atom it abstracts is close to 2.23 eV at the reaction threshold. This is a further indication of the spectator nature of the C_2D fragment in the reaction.

*Abstracted from a paper to be published in *J. Chem. Phys.* and LBL-1101.

3. DYNAMICS OF THE $O^+ - H_2$ REACTION. I: REACTIVE SCATTERING OF $O^+ (^4S_{3/2})$ AT RELATIVE ENERGIES BELOW 15 eV

Keith T. Gillen, Bruce H. Mahan, and
John S. Winn

We have made extensive measurements of the ion product velocity vector distributions for the reaction $O^+(H_2, H)OH^+$ and its isotopic variations. Figure 1 shows a contour map of the product intensity in the barycentric system which clearly indicates that the reaction proceeds by a direct interaction mechanism, rather than through a long-lived H_2O^+ intermediate complex. Spectator stripping is a prominent feature of this and other product distributions obtained at low (< 8 eV) relative energies of collision.

Figures 2 and 3 show, respectively, the OH^+ and OD^+ obtained from $O^+ - HD$ collisions at a relative energy of 11.9 eV, and illustrate a number of the features which characterize the reaction at high relative energy. In both instances, the peak at the spectator stripping velocity has disappeared, since at these energies the ground state OH^+ and OD^+ formed by spectator stripping would be sufficiently internally excited to be unstable with respect to dissociation. The propensity for OH^+ to be formed at angles less than 90° , and OD^+ to occur at angles greater than 90° , is a consequence of general kinematic con-

Fig. 1. A contour map of the intensity of OH^+ from the $O^+ - H_2$ reaction at 4.5 eV relative energy. The small cross locates the velocity of OH^+ formed by the spectator stripping process. (XBL 727-6542)

Fig. 2. A contour map of the intensity of OH^+ formed from $O^+ - HD$ collisions at 11.9 eV relative energy. Note the absence of an intensity peak at the stripping velocity (marked by a small cross), the substantial intensity at velocities inside the $Q = -4.5$ eV circle, and the high intensity at angles less than 90° . (XBL 727-6588)

Fig. 3. A contour map of the intensity of OD^+ formed from $O^+ - HD$ collisions at a relative energy of 11.9 eV. Note the propensity for backscattering, that is, formation of products at angles of 90° or greater. (XBL 727-6593)

siderations which apply to collinear or nearly collinear collisions. The appearance of some product in regions inside the $Q = -4.5$ eV circle, where ground state OH^+ or OD^+ would be unstable with respect to dissociation, is indicative of the formation of $\text{OH}^+(\Delta)$ or $\text{OD}^+(\Delta)$ in some fraction of the collisions.

* Abstracted from a paper submitted to J. Chem. Phys., and LBL-1429.

4. DYNAMICS OF THE $\text{O}^+ \text{H}_2$ REACTION. II: REACTIVE AND NON-REACTIVE SCATTERING AT RELATIVE ENERGIES ABOVE 15 eV

Keith T. Gillen, Bruce H. Mahan, and John S. Winn

We have studied the reactive and non-reactive scattering of O^+ from H_2 , D_2 , and HD at relative energies of collision ranging from 15 to 50 eV. A most striking feature appears in the non-reactive scattering, as is illustrated in Fig. 1. While the small-angle scattering ($\theta < 45^\circ$) has a clear elastic component, the scattering at larger angles is very inelastic. In particular, the intensity ridge found at 70° and larger angles lies approximately on a circle which would be the locus of elastic scattering

from free D atoms. Similar results are found for the other isotopic targets H_2 and HD . In the latter case, two inelastic features can be discerned in the high energy experiments, one coming from scattering of apparently free H, the other from apparently free D.

These phenomena indicate that at energies above 15 eV, the collisions of O^+ with H_2 , D_2 , and HD are essentially impulsive in nature. Therefore, both the non-reactive and reactive scattering should be described to a good approximation by a model in which the three particles interact via hard sphere potential functions. We are currently exploring the predictions of this model, and the initial results show encouraging agreement with experiment.

5. AN APPARATUS FOR THE STUDY OF ION-MOLECULE REACTIONS AT LOW RELATIVE COLLISION ENERGIES

James A. Fair and Bruce H. Mahan

We have constructed an apparatus which allows us to determine the velocity vector distributions of the ionic products of ion-molecule reactions carried out with ion projectile energies between 5 and 20 eV in the laboratory system. This apparatus thus allows us to extend the range of our collision dynamics experiments to significantly lower energies than has been previously possible in our laboratory.

The apparatus consists of a small 90° magnetic mass spectrometer to prepare the primary ion beam, a scattering cell or crossed supersonic molecular beam to provide the target molecules, and a Wien filter-quadrupole mass filter combination for the velocity and mass analysis of the products. Our first experiments on the $\text{N}^+(\text{H}_2, \text{H})\text{NH}^+$ reaction indicates that this process occurs largely by a direct interaction mechanism even at relative energies as low as 1 eV.

6. RESEARCH PLANS FOR CALENDAR YEAR 1973

Bruce H. Mahan

We will continue our studies of the reactive scattering of simple ions ($\text{O}^+, \text{N}^+, \text{C}^+, \text{CO}_2^+$) by small molecules in an effort to learn how to anticipate reaction dynamics from the properties of reactants and products. Studies of the reactions of metastable electronically excited ions have begun, and will be continued. Investigations of the reactions of

Fig. 1. A contour map of the intensity of O^+ scattered from D_2 at an initial relative energy of 20.1 eV. All scattering inside the circle labeled $Q = -4.5$ eV is inelastic enough to cause dissociation of the hydrogen. The circle labeled elastic $\text{O}^+(\text{D}_2, \text{D})\text{O}^+$ gives the locus that O^+ would have if it had been scattered off free D atoms. (XBL 727-6587)

metallic ions will be initiated. We have begun the design and will continue the development of a fast cross-correlation method for the velocity analysis of ion-molecule reaction products. All these projects are aimed at increasing our general understanding of chemical reactions, and specifically at clarifying the higher energy charged particle collision phenomena which are important in discharges, atmospheric and re-entry phenomena, and radiation chemical systems.

7. 1972 PUBLICATIONS AND REPORTS

Bruce H. Mahan and Associates

Journals

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4. Bruce H. Mahan, Recombination of Gaseous Ions, Advan. Chem. Phys. 23, 1 (1973).

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LBL reports

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William H. Miller, Principal Investigator

1. SEMICLASSICAL QUANTIZATION OF NON-SEPARABLE SYSTEMS

William H. Miller and Jimmie D. Doll

The utility of the semiclassical, or WKB, eigenvalue relation for one-dimensional eigenvalue problems is well known. Not only does it provide a useful approximation for the energy levels of a potential well (cf. the Dunham expansion for vibrational eigenvalues), but it can also be "inverted" (the Rydberg-Klein-Rees method) so that the potential function itself can be determined if the energy levels are obtained experimentally (e.g., from spectroscopy).

In light of this success of the semiclassical approximation for systems with only one degree of freedom, and also in view of its usefulness in scattering problems, it seems worthwhile to explore the possibility of extending it to systems with several non-separable degrees of freedom. The desire is to facilitate the analysis of the eigenvalue spectrum of multidimensional systems, the ultimate goal being the establishment of "inversion relations" whereby one could use the experimentally observed vibrational spectrum of a triatomic molecule, for example, to construct its multidimensional potential energy surface.

The first of these goals has been accomplished, i.e., the generalization of the WKB quantum condition to general non-separable systems.¹ The semiclassical eigenvalue relation for a system of N degrees of freedom is related to the periodic classical trajectories of the system: if there are no constants of the motion other than the total energy itself, then there is typically just one periodic orbit for each energy E , and the quantum condition is

$$n(E) + L/4 = h^{-1} \int_0^{\tau} dt \sum_{i=1}^N p_i(t) \dot{q}_i(t). \quad (1)$$

In Eq. (1) $\{q_i(t), p_i(t)\}$ are the coordinates and momenta along the periodic trajectory of energy E , τ is the period of this orbit, h is Planck's constant, and L is a specifically determined integer. Equation (1) defines the function $n(E)$ for all values of the total energy E in terms of the action integral along the periodic trajectory of energy E ; the eigenvalues are $E(n)$, $n = 0, 1, 2, \dots$,

where $E(n)$ is the inverse function of $n(E)$ from Eq. (1).

Because of the difficulty of applying the above result, a semiclassical perturbation expansion for the eigenvalues of an N -dimensional system was carried out;² explicit expressions were obtained for the first- and second-order perturbation energies.

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2. PENNING IONIZATION OF HYDROGEN ATOMS BY METASTABLE HELIUM ATOMS*

W. H. Miller, Charles A. Slocumb, and Henry F. Schaefer

Detailed calculations have been carried out for the Penning and associative ionization of ground state H atoms by $1s2s^3S$ metastable He atoms,

Fig. 1. The potential energy curves for $\text{He}_2\text{-H}(^2\Sigma)$ and $\text{He-H}^+(^1\Sigma)$. (XBL 716-6862)

Fig. 2. The autoionization width of the metastable state He^*-H as a function of internuclear distance. (XBL 716-6860)

Fig. 3. The solid curves are the total ionization cross section (upper curve) from reactions (1) and (2), and the associative ionization cross section (lower curve) separately [reaction (2)], as a function of collision energy. (XBL 716-6859)

Fig. 4. The percentage of the total ionization cross section that yields associated product HeH^+ , as a function of relative collision energy. (XBL 716-6858)

Figure 1 shows the potential energy curves for He^*-H and $\text{He}-\text{H}^+$ that were calculated previously,¹ and Fig. 2 shows the autoionization width Γ as a function of the He^*-H distance. (Γ has units of energy; the autoionization rate is $\Gamma/\hbar$.)

From the quantities in Figs. 1 and 2 it is possible to calculate the cross section for reactions (1) and (2) and the energy distribution of the ionized electrons as well.² Figure 3 shows the total ionization cross section [the sum of cross sections for reactions (1) and (2)] and the associative part separately, and Fig. 4 shows explicitly the associative fraction as a function of the collision energy.

Recent measurements of the associative ionization cross section by Neynaber³ give an energy dependence of the cross section just at that in Fig. 3 and an absolute cross section of 0.22 Å^2 at 1 eV collision energy; as seen from Fig. 3, this is in essentially exact agreement with our calculation. Measurement of the energy distribution of the ionized electrons by Hotop et al.⁴ also shows good agreement with our results for this quantity.

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3. ANALYTIC CONTINUATION OF CLASSICAL MECHANICS FOR CLASSICALLY FORBIDDEN PROCESSES IN INELASTIC AND REACTIVE SCATTERING

Thomas F. George, Jimmie D. Doll, and William H. Miller

A particularly important aspect of the semiclassical theory of molecular collisions is the ability to extend or analytically continue classical mechanics in such a way as to describe collision processes that lie beyond the framework of ordinary classical

mechanics. The most familiar example of such a process is tunneling of a particle through a one-dimensional potential barrier, so that "classically forbidden" transitions in systems with more than one degree of freedom are a generalization of one-dimensional tunneling.

The primary accomplishment of this past year was to show how one can compute these analytically continued classical trajectories (which are necessarily complex-valued) by direct integration of the classical equations of motion much as one does for ordinary classical trajectories. The first application was made to vibrational excitation in the simple collinear $A + BC$ collision,¹ and it was found that one could obtain transition probabilities as small as 10^{-11} (the smallest available for comparison) with excellent agreement (within a few %) with accurate quantum mechanical values. These results are of great practical importance, for vibrational transitions are typically weak. Application has also been made² to rotational-vibrational transitions for fully three-dimensional collisions of He and H_2 , again with excellent agreement with quantum calculations.

Another example of a classically forbidden process is reactive tunneling; this feature

Fig. 1. Reaction probability for the ground state to ground state $H + H_2 \rightarrow H_2 + H$ reaction as a function of relative collision energy. The crosses and circles are the results of different quantum calculations by other workers. (XBL 723-6065)

Fig. 2. Coordinate trajectories for collision energies 0.20 eV (dotted line) and 0.02 eV (dash-dot line). For reference, the dashed line is the "reaction path" and the cross marks the saddle point. R_q and r_a are the translational and vibrational coordinates, respectively, for the arrangement $A + BC$. (XBL 724-6181)

dominates the important threshold region in cases for which there is an activation barrier for the reaction. Complex-valued classical trajectories have been computed for the collinear $H + H_2$ reaction at energies below the classical threshold.^{3,4} Figure 1 shows the ground state reaction probability as a function of collision energy; the circles and crosses are the quantum mechanical results of two different workers, showing excellent agreement with the semiclassical results. (Below 0.21 eV the purely classical cross section is identically zero.) Figure 2 shows the real part of the tunneling trajectory at two different collision energies, illustrating the fact that the sub-threshold dynamics "cuts the corner" of the potential barrier. Semiclassical evaluation of a Boltzmann temperature average shows that this energy region below the classical threshold is the most important for temperatures below 1000°K.

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4. SEMICLASSICAL THEORY OF ELECTRONIC TRANSITIONS IN LOW ENERGY ATOMIC AND MOLECULAR COLLISIONS INVOLVING SEVERAL NUCLEAR DEGREES OF FREEDOM*

William H. Miller and Thomas F. George

The semiclassical theory of electronic transitions in low energy atom-atom collisions is to a large extent a solved problem, the reason being that such transitions have significant probabilities only if there is a crossing, or avoided crossing of potential curves. This paper shows how electronic transitions can be treated in a similar manner for cases, such as an atom-diatom collision, that involve rotation and vibrational degrees of freedom in addition to translation.

More specifically, it is shown how one can combine a classical description of all heavy-particle degrees of freedom (rotation, vibration, and translation) with a quantum-state description of the electronic degrees of freedom; furthermore, this can be done without the necessity of incorporating any dynamical approximations into the theory (other than the semiclassical approximation to the electronic transition). If certain approximations are made, however, the general theory becomes essentially equivalent to the "surface hopping model" used by Tully and Preston;¹ certain features in this model are thus clarified and put on a firmer foundation.

The indications are that this theory should provide an accurate description of electronic transitions in low energy molecular collisions.

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5. RESEARCH PLANS FOR CALENDAR YEAR 1973

William H. Miller

Ways are being explored for simplifying the application of classical S-matrix theory to molecular collisions. In particular, ways will be developed to combine a Monte Carlo treatment of some degrees of freedom while others are quantized semiclassically. This will greatly simplify the application of the theory to three-dimensional collision systems, both reactive and non-reactive. Emphasis will continue to be placed on

classically forbidden collision phenomena, since this is the case for which semiclassical theory makes its most important and rather unique contribution.

Further development of the semiclassical theory of electronic transitions is needed, and applications to some specific systems are being planned. Of special interest is the relationship between the intersecting potential energy surfaces and the coupling between electronic energy with rotation and vibrational energy. Collisions involving electronic transitions are most common when one of the colliding species is in an electronically excited state, usually a metastable state that does not decay too fast radiatively. Thus many of the applications of this general theory will deal with quenching of metastable electronic species, such as

where N_2^* denotes vibrational excitation of the ground electronic state of N_2 .

6. 1972 PUBLICATIONS AND REPORTS

William H. Miller and Associates

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7. T. F. George and W. H. Miller, Complex-Valued Classical Trajectories for Linear Reactive Collisions of $H + H_2$ Below the Classical Threshold, J. Chem. Phys. 56, 5722 (1972) (LBL-813).
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9. T. F. George and W. H. Miller, Open-Channel Projectors for Rearrangement Processes in Molecular Collisions, Phys. Rev. A, 6, 1885 (1972) (LBL-823).
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2. W. H. Miller, Semiclassical Theory of Inelastic and Reactive Scattering, Symposium on Bimolecular Reactions as Elementary Processes, Oberwolfach, Germany, September 27-29, 1972.

LBL reports

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3. S. A. Augustin, P. K. Pearson, H. F. Schaefer and W. H. Miller, Potential Curves and Inelastic Cross Sections for Low Energy Collisions of O^+ and He, LBL-1187 (submitted to J. Chem. Phys.).

Rollie J. Myers, Principal Investigator

1. MOLECULAR FIELD CORRECTIONS FOR ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY

Michael R. St. John and Rollie J. Myers

A number of recent workers have observed the EPR spectra of transition-metal ions, such as Cu^{2+} which have been substituted into a host lattice that is paramagnetic instead of diamagnetic. One example is our work¹ on Cu^{2+} substituted into $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. In our work we found the EPR absorption of the Cu^{2+} to be shifted in field. It is also possible to find a broadening of the absorption if the temperature is raised above 2°K. Other workers have observed both a broadening and a shift in other lattices. While the Cu^{2+} in $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ does not quite follow a spin Hamiltonian, it is possible to assign the spectrum by using an anomalous set of g values. In his thesis,¹ Jindo attempted to correct these g values by utilizing the molecular field parameter that was previously established for Ni^{2+} in $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. While Jindo's method goes somewhat toward lowering the g values down to the diamagnetic values observed in $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$, it does not make sufficient correction. The results of Jindo's method and our new molecular field method are shown in Table I.

In our method the single ion Hamiltonian is written down along with the exchange terms. The exchange is assumed to be isotropic, and only nearest neighbor ions are considered as interacting. The average spin of the neighboring ions is then replaced by a factor proportional to the magnetization. This can be seen as follows:

$$\langle \frac{dE}{dH} \rangle = - \langle \mu \rangle = g\beta \langle S_z \rangle$$

The above equation gives

$$\langle S_z \rangle = 1/g\beta \langle \frac{dE}{dH} \rangle$$

If we use this result to establish the molecular field correction for each of four nearest neighbors, the result for the Cu^{2+} is

$$g(\text{obs.}) = g(\text{dia.}) - \frac{8J}{g\beta^2 H} \langle \frac{dE}{dH} \rangle$$

In this equation J is the exchange interaction parameter from

$$K(\text{exch.}) = - 2J\vec{S}(\text{Ni}) \cdot \vec{S}(\text{Cu})$$

In our calculation we used the normal angle ϕ and adjusted J to obtain the best fit. This gave $J = 0.071 \text{ cm}^{-1}$

The $\alpha\text{-Ni SO}_4 \cdot 6\text{H}_2\text{O}$ lattice is particularly simple in that below 1.5°K only one magnetic sublevel contributes to $\langle dE/dH \rangle$. Above 2°K two sublevels are populated and $\langle dE/dH \rangle$ has a time dependence which will also lead to spin relaxation. This has been observed.

We hope to examine the molecular field method in greater detail so that we will not only be able to test its accuracy, but also to test the nearest-neighbor model as well.

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Table I. Molecular Field Corrections for Cu^{2+}

Mag. field orientation	Observed g value	Correct g value (Jindo)	Correct g value (ours)	g value ZnSeO_4
A axis	2.681	2.372	2.172	2.179
C axis	2.491	2.337	2.283	2.278
γ axis (L)	2.489	2.200	2.083	2.098
γ axis (γ)	2.850	2.530	2.241	2.260

2. ELECTRON PARAMAGNETIC RESONANCE SPECTRUM OF $\text{Ti}(\text{H}_2\text{O})_6^{3+}$

Richard C. Wilson and Rollee J. Myers

Previous work on $\text{Ti}(\text{III})$ has indicated that its EPR spectrum could only be detected at very low temperatures. Such observations are consistent with a $(3d)^1$ ion in a coordination site with only small distortions from octahedral. As a result, we were naturally surprised last year when we observed an EPR spectrum for $\text{Ti}(\text{III})$ in aqueous solutions at room temperature. Since the important species in such solutions is an octahedral $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ this observation was quite unexpected.

To confirm the fact that our spectrum was not due to a complexed or hydrolyzed $\text{Ti}(\text{III})$ we used both HCl and HSO_3CF_3 to provide variable amounts of strong acid. In addition, we cooled these acidic solutions until they formed a glass. From this we observed a simple EPR spectrum characteristic of a randomly orientated species which follows an axial spin Hamiltonian with $g_{\parallel} = 1.98$ and $g_{\perp} = 1.91$.

At room temperature, acidic solutions of $\text{Ti}(\text{III})$ give a single broad line about 2000 gauss wide. As the temperature is lowered, the line width decreases, and at about 228°K the line becomes asymmetric due to the anisotropy of the g tensor. Measurements of the line width were made in the temperature range from 213 to 288°K on various acidic solutions. For each solution, an Arrhenius plot of line width versus temperature resulted in a straight line (see Fig. 1). Least squares fitting of a straight line to the experimental data gave an activation energy of $1800 \pm 50 \text{ cm}^{-1}$. An unusual feature is that no discontinuity occurs at the melting point of the solutions.

Since both $g_{\parallel}$ and $g_{\perp}$ are close to 2.00, we can conclude that the orbital degeneracy associated with the $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ must be split by over 1000 cm^{-1} . Since there are no lattice distortions to be expected in solution, we are forced to conclude that the $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ has a Jahn-Teller distortion which splits the orbital degeneracy by this large amount. If we use the simple formula

$$g_{\perp} = 2.00 - \frac{2\lambda}{\delta},$$

the g values indicate a distortion of about $2,000 \text{ cm}^{-1}$.

This conclusion is consistent with the observed broadening, for what we appear to be seeing is relaxation through one of the spin-

Fig. 1. Line width plot for $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ in water acidified with HCl . Solid points are for solution and open points are for solution frozen into a glass. The line represents the least squares fit to a straight line for the natural logarithm of the line width in gauss vs. $1000/T$ ($^{\circ}\text{K}^{-1}$). (XBL 731-2040)

orbit excited states. This process is known as resonant relaxation.¹ Relaxation of this type requires absorption of a lattice vibration, causing a transition to a real excited state and then relaxation to the ground state through emission of another lattice vibration. If resonant relaxation is the predominant relaxation process, the line width should be proportional to $\exp(-\delta/kT)$, where δ is the energy separation between the ground state spin doublet and the excited state through which relaxation is occurring. From our data, we are seeing relaxation through an excited state 1800 cm^{-1} above the ground state. Possible sources of lattice vibrations in the region of 1800 cm^{-1} are distortion modes of the octahedral shell of water molecules in the complex. Resonant relaxation is also frequency independent. Experiments are planned at other frequencies to test whether this is true of the relaxation we are observing.

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3. PROTON NUCLEAR MAGNETIC RESONANCE ON SOLUTIONS OF TRANSITION-METAL IONS

Thomas M. Hynes and Rollie J. Myers

A number of transition-metal ions have very short electron spin relaxation times in solution. These ions cannot be studied by the usual electron paramagnetic resonance techniques, but in some cases the proton NMR of these solutions can depend upon electron spin relaxation. With this aim in mind we have done proton NMR on $\text{Co}(\text{H}_2\text{O})_6^{2+}$ and $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ in water solutions.

For the species $\text{Co}(\text{H}_2\text{O})_6^{2+}$ we have measured the transverse spin relaxation times of bulk water protons in dilute aqueous solutions of $\text{Co}(\text{ClO}_4)_2$ at 60 MHz and 100 MHz and at temperatures from -35 to $+84^\circ\text{C}$. Low temperatures were achieved by using a solution which was also 2.46 molar in $\text{Ca}(\text{ClO}_4)_2$. Our aim has been to determine T_{2M} , the transverse relaxation time of protons in the first coordination sphere of the hydrated cobalt ion, over a range of temperatures and fields. This relaxation arises due to the dipolar coupling of the proton with the electronic spin,¹ and its rate is governed by the magnitudes of T_1 and T_2 of the electronic spin.²

At temperatures above about 60°C , the transverse relaxation time of the bulk water protons is directly proportional to T_{2M} (T_{2M} region). At lower temperatures this bulk proton relaxation time is also affected by a $\Delta\omega$ mechanism, in which protons lose phase coherence by jumping between the magnetically different bound and bulk environments.³ This effect was not observed in earlier work.^{4,5} At temperatures below about -30°C , bulk proton relaxation begins to be rate limited by the exchange rate of protons between the bound and bulk environments. By comparison with ^{17}O work,⁶ the proton and water exchange rates appear to be equal in unacidified solutions.

Despite the competing effects, values for T_{2M} may be obtained at all temperatures by using the equations of Swift and Connick,³ the water exchange rates of Chmelnick and Fiat,⁶ and the proton-cobalt scalar coupling constant of Matwiyoff and Darley.¹ However, determinations of T_{2M} in unacidified solutions are less exact at lower temperatures, where the $\Delta\omega$ and chemical exchange effects become relatively more important. For this reason we also made measurements on a solution of $\text{Co}(\text{II})$ in 5.27 M HClO_4 . By increasing the proton exchange rate, the $\Delta\omega$ and chemical exchange effects were reduced, and the T_{2M} region was extended to somewhat lower temperatures.

Fig. 1. The ratio, P_M , of coordinated protons to total protons in Ni^{2+} solutions times T_{2P} , the transverse relaxation time of the bulk protons is plotted vs. the reciprocal of the absolute temperature. (XBL 731-2041)

Similar measurements have been made on dilute solutions of $\text{Ni}(\text{ClO}_4)_2$. Again, the relaxation of protons in the first coordination sphere of the hydrated nickel ion is dominated by dipolar coupling.⁷ At temperatures above room temperature the relaxation time of the bulk water protons is directly proportional to T_{2M} . At lower temperatures in unacidified solutions the bulk proton relaxation is rate limited by chemical exchange of protons. This proton exchange rate can be dramatically increased by the presence of acid⁸ and measurements were also made on a solution of $\text{Ni}(\text{II})$ in 5.27 M HClO_4 as shown in Fig. 1. This extended the T_{2M} region far

below 0°C. Curve fitting and the establishment of relaxation times for both ions awaits measurements at 220 MHz.

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4. RESEARCH PLANS FOR CALENDAR YEAR 1973

Rollie J. Myers

The molecular field model will be used to modify the usual spin Hamiltonian for the presence of interacting ions. As a test case for ions with zero-field splittings we will apply this method to Mn^{2+} in $NiSO_4 \cdot 6H_2O$. We will also apply our method to previously published EPR results done by other workers.

Further measurements will be made on $Ti(H_2O)_6^{3+}$ and similar hydrated transition-metal ions. This work will include both NMR

and EPR which will be designed to determine the mechanisms for electron spin relaxation.

Our electron-electron double resonance experiments will be continued so that we can obtain direct evidence of the relative importance of dipole-dipole and exchange interaction for interacting free radicals. In addition, we plan to use our previously developed electrolytic reduction technique to do EPR work on some usual radical species in solution.

5. 1972 PUBLICATIONS AND REPORTS

Rollie J. Myers and Associates

Journals

1. A. Jindo and Rollie J. Myers, Electron Exchange for Hydrated Ions in the $\alpha-NiSO_4 \cdot 6H_2O$ Lattice--Electron Paramagnetic Resonance Study of Hydrated Transition-Ions in $ZnSeO_4 \cdot 6H_2O$, J. Mag. Res. 6, 633 (1972).
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Kenneth S. Pitzer, Principal Investigator

1. SOLUTIONS OF ELECTROLYTES

Kenneth S. Pitzer and Guillermo D. Mayorga

The general objective of this program is the prediction of the thermodynamic properties of electrolytes with high accuracy from a minimum number of readily measured parameters. The equations are selected in the light of modern statistical mechanical theories in a manner such that each parameter has general physical meaning but need not necessarily be defined in terms of a detailed molecular model.

More specifically, it has been shown from an improved statistical treatment based upon the Debye-Hückel ion distribution function that the effect of short-range forces between pairs of ions, i.e., the second virial coefficient, should depend also on the ionic strength. Numerical calculations on more realistic models confirm this general effect

in which second virial coefficients for pure electrolytes decrease rapidly with increase in ionic strength in the very dilute region yet become nearly constant at higher concentrations. This pattern of behavior was known experimentally and seemed puzzling heretofore.

By including the appropriate ionic strength dependence in the second virial coefficients, a relatively simple system of equations for the thermodynamic properties of electrolytes is developed. These equations are shown to represent experimental behavior to much higher concentration than any previous system of comparable complexity. In the first report numerical parameters and comparisons with experimental data are given for the osmotic coefficients of several pure electrolytes, for the activity coefficients of a series of mixtures HCl-MCl, and for the osmotic coefficient for all possible mixtures of sodium and potassium chlorides and nitrates. The last comparison is shown in Fig. 1, where $\Delta\phi$ is the difference in the osmotic coefficient of the mixed electrolyte from the appropriately weighted mean for the pure components at the same ionic strength. The curves for NaCl-KNO₃ and KCl-NaNO₃ are predicted from theory and parameters determined from the pure electrolytes and mixtures with a common ion, and these curves agree satisfactorily with the measured points.

In later work (after the first report) all the experimental data for osmotic or activity coefficients of aqueous pure electrolytes at room temperature have been analyzed and the resulting tables of parameters will be published soon. There is good agreement with the general equations, even for 4-1 and 5-1 electrolytes. For 2-2 and 2-3 electrolytes it is necessary to include an additional term, still within the same system of equations, after which agreement is also very good.

2. OTHER TOPICS

Lawrence S. Bernstein, Janice J. Kim, and Gerald J. Vogt

These graduate students have just begun research on topics which are discussed in the next section.

Fig. 1. The difference in osmotic coefficient of mixed electrolytes from pure components at the same ionic strength. The curves for NaCl-KNO₃ and KCl-NaNO₃ are calculated with parameters from pure electrolytes and mixtures with a common ion.

(XBL 725-6295)

3. RESEARCH PLANS FOR CALENDAR YEAR 1973

Kenneth S. Pitzer

a. Solutions of Electrolytes

The theoretical program will continue with primary emphasis on mixed aqueous electrolytes. In addition x-ray scattering measurements will be made for a few pure solutes with very heavy ions in an effort to provide a direct experimental test of the radial distribution functions calculated theoretically.

b. Nuclear Spin Species of Methane

The heat capacity of solid methane below 10°K shows anomalous properties presumably associated with conversion of nuclear spin species. This quantity will be measured under conditions providing better control of such spin-species conversion processes in an effort to understand these interesting effects.

c. Anomalous Internal Motions in Molecules

The molecule XeF_6 is known to differ greatly from other hexafluorides, which are simple octahedral molecules. But XeF_6 does not display the properties expected for any

plausible static deformation. Previous concepts of pseudorotation and inversion are being generalized from one to three dimensions in an attempt to find a model conforming to the peculiar properties of XeF_6 . The relationship of these peculiarities to the atomic structure of xenon will also be considered, and this study may lead to consideration of other differences of heavy atoms from the lighter members of the same group in the periodic table.

4. 1972 PUBLICATION AND REPORT

Kenneth S. Pitzer

Journal

1. K. S. Pitzer, Thermodynamic Properties of Aqueous Solutions of Bivalent Sulfates, J. Chem. Soc. Faraday Trans., II, 68, 101 (1972)

LBL reports

1. Kenneth S. Pitzer, Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations, LBL-846, May 1972 (accepted for publication, J. Phys. Chem.).

E. NUCLEAR SCIENCE

Donald R. Olander, Principal Investigator

1. LASER VAPORIZATION OF SOLIDS

Robert A. Olstad and Donald R. Olander

The laser-induced vaporization of iron and of a binary solid compound, zirconium hydride, was studied using a quadrupole mass spectrometer. A Q-switch ruby laser with pulse width of 80 nanoseconds was used to heat zirconium hydride samples under high vacuum to temperatures up to 2500°C. The mass spectrometer ionizer was located in a line-of-sight path 40 cm from the target. By an analysis of the measured mass spectrometer signals, the instantaneous rate of vaporization of hydrogen during the rapid temperature transient could be determined.

Application of an equilibrium model to the vaporization process predicts that predominantly H_2 (rather than H-atoms) should be emitted. The vaporized H_2 should have a Maxwellian velocity distribution characteristic of the instantaneous surface temperature, and the rate of vaporization should be related to the H_2 vapor pressure by the Langmuir equation. Since the H_2 vapor pressure is a function of both surface temperature and surface hydrogen concentration, it was necessary to solve simultaneously the time-dependent heat conduction and hydrogen diffusion equations in the heated zirconium hydride in order to predict the vaporization rates.

It was found that H-atom and H_2 molecules were emitted at thermal equilibrium with the surface. At low laser power density, the magnitude of the H_2 signals agreed with the equilibrium model. At high laser power density, the magnitude of the H_2 signals was less than predicted, possibly because of a diffusion barrier at the surface. The H-atom signals were much larger than predicted, indicating that they were produced by a non-equilibrium surface process.

Conventional mode laser pulses (1 msec duration) were used to vaporize iron samples. The measured mass spectrometer signals were in agreement with equilibrium calculations if the flow of molten iron was taken into account.

2. A MODULATED MOLECULAR BEAM STUDY OF THE ENERGY OF SIMPLE GASES SCATTERED FROM PYROLYTIC GRAPHITE*

Wigbert J. Siekhaus, James A. Schwarz and Donald R. Olander

The energy of rare gases and several diatomic gases after scattering from pyrolytic graphite was determined by molecular beam-phase sensitive detection methods. The angle of incidence of the molecular beam and the angle of sampling of the reflected molecules were both fixed at 45°. The phase shifts induced by changing either the temperature of the incident gas or the solid were utilized to determine an apparent temperature of the scattered molecules.

The results showed that the apparent temperature of the reflected molecules was independent of the temperature of the incident gas. With increasing solid temperature, the reflected gas temperature increased up to a limiting value which was dependent on the gas and the surface only. Both the basal and prismatic faces of graphite were investigated. In addition, a prism plane specimen which had not been subjected to high temperature heat treatment was studied. The apparent temperature of the reflected beam did not depend upon the crystallographic face of the graphite but was markedly reduced by high temperature annealing.

* Abstract of paper published in Surface Science 33, 445 (1972).

3. MOLECULAR BEAM SURFACE REACTIONS-WATER VAPOR ON GRAPHITE

Rajarama T. Acharya, Donald R. Olander, and Alan Ullman

The modulated molecular beam technique has been applied to investigate the surface reactions which occur when a beam of H_2O strikes a heated graphite surface. The amplitudes and phase shifts of the reaction product signals (CO and H_2) have been measured as a function of surface temperature, chopping frequency, and beam intensity.

The signal amplitudes indicate that the H_2O reaction at the annealed prism plane of pyrolytic graphite becomes large (i.e., reaction probability of $> 10^{-3}$) only at solid temperatures above 2000°K. Comparable reaction probabilities for the O_2 -graphite reaction were attained at considerably lower temperatures. The CO phase shift in the H_2O -C reaction approaches a limiting value as the chopping frequency is reduced, which indicates that the reaction is primarily influenced by a diffusional step rather than by a surface chemical reaction. However, the asymptotic value of the phase lag is in between that of a simple diffusional process (45°) and a double diffusion mechanism followed by the O_2 -C reaction ($22\frac{1}{2}^\circ$).

The apparent reaction probability of CO is as much as an order of magnitude smaller than that of the other reaction product, H_2 , which suggests that the surface processes leading to CO production are more strongly diffusion-controlled than those which produce H_2 . Experiments with variable beam intensity demonstrated that the reaction is first order in H_2O pressure at the surface. The H_2O -C reaction is considerably more complex than the O_2 -C reaction and the mechanism of the former has not yet been deduced from the data.

4. VISCOSITY OF CESIUM UP TO 1600°C

Han-Chung Tsai and Donald R. Olander

The viscosity of liquid cesium has been measured by the oscillating crucible method to within 150°C of the critical temperature. Because of the high vapor pressure of cesium at temperatures above 1000°C, a massive "pressure-vessel" type of oscillating crucible was employed. Since the crucibles can only be partially filled with liquid, the space above the interface contains cesium vapor at high pressure. Consequently, the frictional drag on the crucible inner walls is in part due to the viscosity of the vapor, and this effect must be considered in extracting the viscosity of the liquid from the data. Since the viscosity of the liquid is $< mP$, special refractory metal alloy torsion wires which have been carefully annealed were used to prevent excessive damping of the oscillating motion due to internal friction. When corrected for vapor drag, the resulting viscosities of liquid cesium are shown as the upper curve in Fig. 1. The lower curve shows the vapor viscosity,

and the middle line represents application of the law of rectilinear diameters to the viscosities of the two phases. After extrapolation of this line by $\sim 150^\circ C$, the viscosity of cesium at the critical point is found to be $0.53 \pm 0.03 mP$.

Fig. 1. Viscosity of liquid cesium and estimation of the critical viscosity by the law of rectilinear diameters. The vapor viscosity is due to Bonilla.

(XBL 731-2157)

5. DIFFUSION IN LIQUID URANIUM

Jack Hovingh and D. R. Olander

The diffusion coefficient and saturation concentration of lanthanum in molten uranium were measured by using a capillary tube technique. Activated lanthanum was placed on top of a uranium ingot in a beryllia capillary tube. The capillary tube was heated to 1200°C, held at temperature for various diffusion times, and cooled. The lanthanum concentration was determined as a function of distance in the uranium from the lanthanum uranium interface by counting the photons emitted by the decay of the activated lanthanum.

The measured diffusion coefficient of lanthanum in molten uranium appears to be at least an order of magnitude less than predicted by theory. The measured saturation concentration of lanthanum in molten uranium appears to be several times higher than previously reported. The higher apparent saturation concentration may be caused by lanthanum seepage into a gap formed between the uranium ingot and the beryllia capillary tube during heating.

6. OXYGEN REDISTRIBUTION IN CERAMIC NUCLEAR FUELS*

Donald R. Olander

The presence of temperature gradients as large as 6000°C/cm in ceramic nuclear fuel elements causes extensive redistribution of the constituents of the fuel. The profile of the concentration of oxygen in solid UO_{2+x} which is held in such a temperature gradient was calculated on the assumption that oxygen transport occurs via diffusion of CO, CO₂, and O₂ along fissures in the solid (carbon is an impurity in uranium which produces CO and CO₂ when the fuel is held at high temperatures). Oxygen redistribution occurs by diffusion of CO₂ from the cold to the hot end, where reduction to CO occurs, followed by back-migration of CO to the cold end. A stationary state is established in the ternary diffusion system consisting of CO, CO₂, and O₂. At each point along the temperature gradient, the equilibrium oxygen pressure is equal to that simultaneously required by the gas phase reaction $CO + 1/2 O_2 = CO_2$ and by the oxygen potential of the fuel, which is a function of the oxygen content. The calculations show that initially uniform hyperstoichiometric fuel approaches perfect stoichiometry (i.e., $UO_{2.00}$) at the cold end and becomes enriched in oxygen at the hot end. The significance of oxygen redistribution to the performance of nuclear fuel elements is that the fuel composition at the cold outer surface of the fuel rod in large part determines the ability of the cladding to withstand corrosive attack by the fuel with which it is in contact.

ture furnace for producing beams of partially dissociated hydrogen has been designed for this experiment.

Construction of the second molecular beam apparatus will be completed. The unique feature of the new device is the horizontal mounting of the target, which permits holding of fragile targets such as wafers of ionic crystals. The system can also be used to study reactions of gaseous beams with liquid targets. This apparatus will be used to study the reaction of fluorine molecular beams with single-crystal uranium dioxide.

The gas phase radiolysis of molecular oxygen by protons from a Van de Graaff accelerator will be completed.

The study of lanthanum diffusion in liquid uranium will continue. In order to obtain more accurate lanthanum penetration profiles than are obtainable by the present method, the detection system has been redesigned to permit continuous counting while diffusion is in progress.

The analytical studies of thermal gradient redistribution in nuclear fuels will be extended to oxygen migration in mixed uranium-plutonium oxides. Uranium vapor transport in mixed hyper-stoichiometric oxides will also be analyzed.

8. 1972 PUBLICATIONS AND REPORTS

Donald R. Olander and Associates

Book chapter

1. D. R. Olander, Technical Basis of the Gas Centrifuge, in *Advances in Nuclear Science and Technology*, Vol. 6 (1972), pp. 105-174.

Journals

1. D. R. Olander, A Chemistry-Materials Program in a Nuclear Engineering Curriculum, *Trans. Amer. Nucl. Soc.* **15**, 57 (1972).
2. D. R. Olander, R. H. Jones, W. J. Siekhaus and J. A. Schwarz, Investigation of Gas-Solid Reactions by Modulated Molecular Beam Mass Spectrometry, *J. Vac. Sci. and Tech.* **9**, 1429 (1972) (LBL-189).
3. D. R. Olander, W. Siekhaus, J. Schwarz and R. Jones, Reactions of Modulated Molecular Beams with Pyrolytic Graphite. Part I - Oxidation of the Basal Plane, *J. Chem. Phys.* **57**, 408 (1972) (LBL-190).

* Abstract of paper published in *J. Nucl. Mater.* **44**, 116 (1972).

7. RESEARCH PLANS FOR CALENDAR YEAR 1973

Donald R. Olander

The modulated beam study of the water vapor-graphite reaction will be extended by utilizing mixed beams of D₂O and H₂O in order to ascertain the extent of isotope mixing in the molecular hydrogen reaction product and in the unreacted water vapor. The accumulated data will be analyzed in order to identify likely reaction mechanisms.

Upon completion of the H₂O-C study, the molecular beam facility will be used to study the reaction of atomic hydrogen with pyrolytic graphite. A high tempera-

4. D. R. Olander, W. Siekhaus, J. Schwarz and R. Jones, Reactions of Modulated Molecular Beams with Pyrolytic Graphite. Part II-Oxidation of the Prism Plane, J. Chem. Phys. 57, 421 (1972) (LBL-191).

5. W. J. Siekhaus, J. A. Schwarz and D. R. Olander, A Modulated Molecular Beam Study of the Energy of Simple Gases Scattered from Pyrolytic Graphite, Surf. Sci. 33, 445 (1972) (LBL-843).

6. D. R. Olander, Oxygen Redistribution in UO_{2+x} , J. Nucl. Mater. 44, 116 (1972) (LBL-801).

7. H. C. Tsai and D. R. Olander, The Viscosity of Molten Uranium Dioxide, J. Nucl. Mater. 44, 83 (1972) (LBL-809).

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1. D. R. Olander, The Viscosity of Molten Uranium Dioxide, American Nuclear Society Meeting, Las Vegas, June 1972.

2. D. R. Olander, A Chemistry-Materials Program in a Nuclear Engineering Curriculum, American Nuclear Society Meeting, Las Vegas, June 1972.

3. W. J. Siekhaus, A Modulated Molecular Beam Study of the Reaction of Oxygen with the Prismatic Surfaces of Pyrolytic Graphite, Eighth International Symposium on Rarefied Gas Dynamics, Stanford, July 1972.

4. J. A. Schwarz, A Modulated Molecular Beam Study of the Energy of Simple Gases Scattered from Pyrolytic Graphite, Eighth International Symposium on Rarefied Gas Dynamics, Stanford, July 1972.

5. D. R. Olander, High Temperature Gas-Solid Reactions by Modulated Molecular Beam Mass Spectrometry, FOM Institute of Atomic and Molecular Physics, Amsterdam, Holland, October 1972.

LBL reports

1. T. R. Acharya and D. R. Olander, The Rate of Oxidation of the Basal and Prismatic Surfaces of Pyrolytic Graphite in the Transition Regime Between Chemical and Diffusional Control, LBL-488, January 1972.

2. D. R. Olander, Oxygen Potential Changes in Mixed Oxide Fuels, LBL-872, June 1972; submitted to Nuclear Technology.

3. D. R. Olander, The Kinetics of Actinide Redistribution and Pore Migration by Vapor Migration in Mixed Oxide Fuels, LBL-1131, August 1972; submitted to J. Nucl. Mater.

4. R. A. Olstad, Mass Spectrometric Investigation of Laser-Induced Vaporization of Binary Solid Compounds (Ph.D. thesis), LBL-1177, December 1972.

II. Metallurgy

A. CRYSTAL IMPERFECTIONS

Jack Washburn, Principal Investigator

1. MECHANISM OF DIPOLE BREAK-UP

Jack Washburn

Breaking of dislocation dipoles in magnesium oxide into strings of prismatic loops has been followed by repeated electron microscope observation of the same areas with intermediate heating of the foil to high temperatures.

The break-up mechanism is shown schematically in Fig. 1. A wave-like pattern starts from both ends of the dipole in the following way: In an initially uniformly spaced dipole vacancies have a higher chemical potential at the ends than at any other place due to line tension. Therefore, on annealing, vacancies at the left of the line MN tend to migrate toward the right. This process increases the spacing at 'a' which results in starting a drift of vacancies also from b to a. This further increases the spacing at a and starts to decrease it at b. The reduced spacing at b then starts a flow of vacancies from b to c. The process repeats toward the middle of the dipole. Thus, a wave pattern is set up which eventually results in breakup of the dipole into a string of loops. As the annealing time increases, the amplitude of the spacing fluctuations increases and the first loop pinches off at 'b', then the next one at 'd' and so on. See dipoles B, D and E in Fig. 2. If the two dislocations in the dipole are not uniformly spaced initially, the effect of non-uniform spacing may cause break-up to start also at interior points. (See dipole A in Fig. 2.)

After break-up, wavelength (λ) can be measured because it is equal to the spacing of the resulting dislocation loops.

Fig. 1. Schematic illustration of dipole breaking by pipe diffusion as the time of annealing is increased. (XBL 725-6220)

Fig. 2. Breaking of dislocation dipoles, $b = 1/2[101]$, on annealing. (XBB 722-1023)

A theoretical analysis¹ based on this model gave a value of 60,500 cal/mol for the activation energy for pipe diffusion of oxygen ions in MgO.

1. J. Narayan and J. Washburn, *Cryst. Lattice Defects* **3**, 91 (1972).

2. THE MECHANISM OF DISLOCATION LOOP COARSENING IN MgO

Jagdish Narayan and Jack Washburn

When magnesium oxide is plastically deformed (bending) most of the damage is introduced in the form of dislocation dipoles. In a thin sheet bent along the $[010]$ axis, dislocation dipoles are introduced on (101) $[\bar{1}01]$, $(\bar{1}01)[101]$ and on $(110)[\bar{1}10]$, $(110)[110]$ slip systems. If the bending axis is slightly off from $[010]$, dipoles on $(011)[111]$ and $(0\bar{1}1)[011]$ also appear. A brief description of the mechanism of dislocation dipole formation follows: moving screw dislocations acquire jogs of both kinds during motion; this results in formation of edge dislocation dipoles trailing behind. Many of the dipoles are terminated, becoming elongated closed loops by the mechanism described by Washburn.¹

As the plastically deformed crystals are heated to successively higher annealing temperatures, the dipoles start breaking up into strings of small circular prismatic dislocation loops. First to break up are the dipoles of smallest spacing. The breaking up into circular loops starts at as low as 850°C, depending upon the separation of the two edge dislocations comprising the dipole. As the time and temperature of annealing is increased, dipoles of larger spacing break up and finally loop coarsening takes place.

Up to now the mechanism of loop coarsening was not clear and was ambiguously attributed to bulk diffusion² because the thin foils for transmission electron microscopy were obtained from different bulk samples, annealed at different temperatures for various amounts of time. To investigate the mechanisms of annealing in more detail, it is necessary to photograph the same area of a single specimen after various annealing treatments.

Experiments of this type have been carried out with the following results. After the breaking of dipoles, many pairs of the resulting coplanar groups of loops, where the separation was small enough for a strong interaction, moved closer together by conservative climb or self climb. Self climb of dislocation loops differs from the usual non-conservative growth or shrinkage in the sense that the total area of the loop projected perpendicular to its Burgers vector remains unchanged and climb occurs by migration of atoms along the easiest path, i.e., the core of the dislocation.

Figure 1 shows two pairs of loops during a set of annealing treatments at 1186 and 1250°C. Assuming that the loop migration took place entirely by pipe diffusion along the circumference of the loops and that the driving force was only the loop-loop interaction energy, an expression for the rate of loop migration was derived.³ Quantitative measurements of the rates of migration of seven loop pairs lead to the following conclusions:

- 1) The activation energy for pipe diffusion and pre-exponential factor $D_0 a^2$ from measurements of rate of self-climb of coplanar pairs of loops, $b = 1/2 (101)$, are $60,300 \pm 3500$ cal/mol and $(7.5 \pm 4.3) \times 10^{-18}$ cm⁴/sec, respectively.
- 2) Self-climb is the primary mechanism of dislocation loop coarsening during annealing of plastically deformed magnesium oxide up to 1250°C.

1. J. Washburn, in *Electron Microscopy and Strengths of Crystals*, edited by G. Thomas and J. Washburn (Interscience, New York, 1963), Chap. 6.
2. G. W. Groves and A. Kelly, *J. Appl. Phys.* **34**, 3104 (1963).
3. J. Narayan and J. Washburn, *Phil. Mag.* **26**, 1179 (1972).

Fig. 1. Self-climb at 1 and 2 at two different temperatures. Some of the smaller loops have slipped out of the foil. Annealing treatments: A+B, 2438 sec at 1186°C; B+C, 2392 sec at 1250°C; C+D, 1570 sec at 1250°C; D+E, 1202 sec at 1250°C; E+F, 2369 sec at 1250°C. (XBB 721-117)

3. PRECIPITATION OF PHOSPHOROUS IN ION IMPLANTED SILICON

Krishna Seshan and Jack Washburn

Ion implantation in silicon is accompanied by damage along the path of each implanted ion which above a critical number of ions per cm² of the order of 10^{14} results in an amorphous layer. On subsequent annealing recrystallization of this layer occurs and

Fig. 1. Weak beam dark field image of a p-type silicon sample irradiated with 2×10^{14} p ions/cm². The foil is oriented for a two-beam case. The linear defects lie along the (110) directions.

(XBB 722-750)

interstitials and vacancies aggregate into defects large enough to be detected by transmission electron microscopy. The present experiments are part of a continuing study of the nature and effects of these defects.

Figure 1 shows a specimen that was implanted with 2×10^{14} phosphorous ions/cm² then heated to 800°C for 1/2 hour. In addition to dislocation loops there are numerous rod-shaped defects that lie along (110) directions. Similar rod-shaped defects have been observed in boron implanted silicon^{1,2} and in silicon implanted with phosphorous at 200°C.³ These rod defects have previously been reported to be absent when phosphorous is implanted at 20°C.^{1,3}

The diffraction contrast effects exhibited by the rods are similar to those described by

Davidson and Bouker.⁴ Dark field and weak beam dark field observations suggest that the defects cannot be simple dislocation dipoles. The type of black-white contrast which appears for rods that lie parallel to the foil surface is also similar to that which is observed for the rod-shaped precipitates in Al-Mg₂Si.⁵

It is found that rod-like defects are absent from n-type silicon of the same dose and heat treatment. This indicates that the small amount of boron, already present, has an important influence on the formation of linear defects. However, the number of boron atoms in the 1 micron thick implantation layer is only about 10^{12} per cm². This alone is insufficient to cause such a high density of defects. Therefore, it was concluded that these rod defects also involve the precipitation of phosphorous.

1. R. W. Bicknell, European Conference on Ion Implantation, IPPS/IEEE, September 1970.
2. L. T. Chadderton and F. H. Eisen, *Rad. Eff.* 7, 129 (1971).
3. M. Tamura, T. Ikeda and Tokuyama, *Proc. Second International Conference on Ion Implantation in Semiconductors*, edited by I. Ruge and J. Graul, (Springer-Verlag, 1971), p. 46.
4. S. M. Davidson and G. R. Booker, *Rad. Eff.* 6, 83 (1970).
5. W. L. Bell and G. Thomas, *Proc. 6th International Congress for Electron Microscopy*, Kyoto (1966).

4. MEMORY STATE FILAMENTS IN As-Te-I AMORPHOUS SEMICONDUCTORS

Jon Roberts

This study investigates the mechanism of growth and the crystalline character of the conductive filaments produced electrically in $\text{As}_{53}\text{Te}_{43}\text{I}_{04}$ amorphous alloy. The filaments begin growth at the positive electrical contact after the material has switched into the conductive state, and grow at a rate proportional to the square root of the duration of power application. The level of applied current has no significant effect on the growth rate, so it is concluded that the driving force for diffusion is the electric field.

The filaments are composed of tellurium crystals, as determined by electron beam microprobe studies. A method of extracting the filaments for electron diffraction studies has been developed, and the results show that the filaments are often single crystals. Continued studies will determine the preferred growth orientation.

5. FIELD ION MICROSCOPE OBSERVATIONS OF LOW TEMPERATURE ION BOMBARDMENT DAMAGE IN IRIIDIUM

Kaj Stolt

Well-annealed Ir specimens are being irradiated at 10°K with 30 kV argon ions in situ in the atom probe FIM described in the previous report. After bombardment the surface damage is removed by field evaporation of a few surface layers, after which the specimen is slowly annealed up to 70°K. During annealing single and double bright spots are seen to pop up on the surface, in the temperature interval 15-70°K, as has been observed previously following

Fig. 1. Annealing sequence showing a cluster emerging on a (100) plane. (XBB 731-277)

proton bombardment of iridium.¹ These spots have been attributed to interstitials migrating to the surface. An additional observation in this study is the appearance of large clusters of bright spots, containing from 3 to as many as 15 spots. One example of a cluster is shown in Fig. 1. The clusters have been observed to pop up on the surface over the same temperature interval as the single and double spots. After emerging, the clusters tend to be stable with further annealing, i.e., no spots disappear when the temperature is increased. This is taken as evidence that the clusters are not due to surface migration of impurity atoms from the shank of the tip. This is also supported by the fact that no clusters have been observed during annealing of unirradiated specimens. Preliminary investigations of the behavior of the clusters with increasing voltage reveal that the spots can be removed one at a time by pulsed field evaporation. This seems to indicate that the spots are due to individual atoms in metastable positions on the surface.

At present an attempt to clarify whether impurity atoms play a role in formation of

the clusters is being undertaken by analyzing the clusters with the atom probe. Investigation of the volume of material immediately beneath a cluster by careful field evaporation should also shed more light on the origin of the clusters.

1. P. Petroff and J. Washburn, A Field Ion Microscope Investigation of 10 MeV Proton Damage in Iridium, Phys. Stat. Sol. 32, 527 (1969).

6. RESEARCH PLANS FOR CALENDAR YEAR 1973

Jack Washburn

1. Electron microscope studies of ion-implanted silicon: Effects of annealing treatments and ion implantation dose on defects in the implanted layer will continue to be investigated for phosphorous-implanted silicon, and the work will be expanded to study arsenic and boron-implanted silicon.

2. Field ion microscopy will be applied to a study of the effect of surface layer atoms on work function. Ni_4W in the ordered state permits surface layers consisting entirely of Ni atoms or of Ni + W to be exposed by field evaporation in certain regions of the field ion microscope tips. Work function measurements will be compared for the two kinds of surfaces.

3. Radiation damage produced by electron bombardment of copper and copper aluminum alloys in the 650 kV electron microscope will be used in a continuing study of dislocation climb phenomena. In particular the effect of stacking fault energy on climb due to capture of interstitial atoms produced by electron irradiation will be investigated. To make these experiments practical it is planned to modify the column of the high voltage microscope to permit use of side entry stages.

4. The possibility of producing a low cost photovoltaic cell based on a sputtered thin film of ZnS will continue to be investigated along with a continuing study of the mechanism of operation of the cuprous sulphide/cadmium sulfide heterojunction solar cell.

5. Memory filaments in amorphous As-Te-I semiconducting glasses have been characterized as whisker-like crystals of Te. However, work still remains to be done before an understanding of their mechanism of growth will be achieved.

7. 1972 PUBLICATIONS AND REPORTS

Jack Washburn and Associates

Journals and book

1. J. Narayan and J. Washburn, Direct Observation of Pipe Diffusion in Magnesium Oxide, Scripta Met. 6, 259-262 (1972) (LBL-476).
2. J. Narayan and J. Washburn, Direct Evidence of Presence of Both Interstitial and Vacancy Dislocation Loops in Plastically Deformed and Subsequently Annealed Magnesium Oxide, Scripta Met. 6, 263-266 (1972) (LBL-475).
3. J. Washburn, Annealing of Loops and Tetrahedra, in Radiation-Induced Voids in Metals (Proc. of the 1971 Internatl. Conf. Albany, N.Y., June 9-11, 1971), edited by J. W. Corbett and L. C. Ianniello, pp. 647-662.
4. E. Nes and J. Washburn, Precipitate Colonies in Silicon, J. Appl. Phys. 43, 2005 (1972) (UCRL-20354 Supp.).
5. J. Narayan and J. Washburn, Pipe Diffusion in Magnesium Oxide, Crystal Lattice Defects 3, 31-98 (1972) (LBL-492).
6. K. Seshan and J. Washburn, On Precipitation of Phosphorous in Ion Implanted Silicon, Radiation Effects 14, 267 (1972) (LBL-493).
7. J. Narayan and J. Washburn, Self-climb of Dislocation Loops in Magnesium Oxide, Phil. Mag. 26, No. 5, 1179 (1972) (UCRL-20335).
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9. J. Narayan and J. Washburn, Pipe Diffusion in Magnesium Oxide, Crystal Lattice Defects 3, 91 (1972) (LBL-492).
10. J. Narayan, On the Termination of Dislocation Dipoles, Phys. Stat. Sol. (b) 54, K1 (1972) (LBL-436).

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1. J. Washburn, Direct Observations of Dislocation Climb, presented at J. Dorn Memorial Symposium, AIME, Cleveland, Ohio, Oct. 16-19, 1972 (LBL-866).

LBL reports

1. J. Narayan and J. Washburn, On the Mechanism of Dislocation Loop Coarsening in MgO (Conservative Climb), LBL-825, March 1972; submitted to J. Am. Ceram. Soc.

2. J. Narayan and J. Washburn, Electron Microscopic Studies of the Micro-Erosion in Brittle Solids, LBL-899, June 1972; submitted to Wear.

3. K. Seshan, W. L. Bell, and J. Washburn, A Rapid Method for Distinguishing Vacancy

and Interstitial Loops in Ion Implanted Crystals, LBL-1103, August 1972; submitted to Physica Status Solidi (A).

4. K. Seshan, W. L. Bell, and J. Washburn, A Rapid Method for Distinguishing Vacancy and Interstitial Loops in Ion Implanted Crystals, LBL-1103, August 1972; submitted to Physica Status Solidi (A).

5. J. Narayan and J. Washburn, Self Diffusion in Magnesium Oxide, Acta Met., in press; LBL-473, Feb. 1972.

B. THEORETICAL METALLURGY

John W. Morris, Jr., Principal Investigator

1. THERMODYNAMICS AND PHASE STABILITY

a. Thermodynamics of Inhomogeneous Systems

John W. Morris, Jr.

Recent research* into the nature of continuous two-phase interfaces in systems obeying the thermodynamics of one-component fluids led to the intriguing result that material near the interface is necessarily subject to a non-classical stress system which includes "multipolar" stresses of tensor order greater than 2. It was shown that despite the mechanical complexity of the interface Gibbs' classical thermodynamics of surfaces follows naturally when the Gibbs construction is used. However, the multipolarity of the stress within the interface did raise questions concerning the proper definition of the "surface stress" and the validity of the claim, based on oversimplified mechanical models, that the "surface stress" of an interface in a simple fluid is equal to its thermodynamic surface tension.

These questions were investigated by using the second-order gradient model, developed by Van der Waals and by Cahn and Hilliard, in which the free energy density at a point within the fluid is assumed to depend on the local temperature, the local mass density, and the local values of the first two gradients of the mass density. The stress system within an interface in such a fluid includes non-zero stresses of tensor order 2, 3, and 4. Nonetheless a scalar thermodynamic pressure may be defined within the interface, and the surface tension is given by the surface excess of this pressure.

The results of this investigation are the following. Let the "surface stress" be defined, as is customary, from the incremental work done in an infinitesimal stretching of the surface which preserves its shape. If the surface is initially flat this "surface stress" is identical to the surface tension. Only the second-order stress does work during a homogeneous stretching; the multipolar stresses maintain the equilibrium density variation normal to the plane of the surface. If the surface is initially spherical the multipolar stresses do non-negligible work during a homogeneous stretching, but the "surface stress" may still be shown to be equal to the surface tension to within terms of order R^{-2} , where R is the radius of curvature.

*J. W. Morris, Jr., J. Chem. Phys. **57**, 769 (1972)

J. W. Morris, Jr. and P. L. DeBruyn, LBL-454 (J. Colloid Interface Science (in press)).

b. Bonding and Phase Stability

Charles W. Krause and John W. Morris, Jr.

The existence of various close-packed phases provides evidence that relatively long-range interatomic forces are acting in a metal. For example, if it is assumed that a central two-body potential determines the crystal structure of a metal, then the range of the potential must extend out to at least third nearest neighbors in order for a crystal to exist in either the hcp or the fcc phase.

This work treats the stability of close-packed structures employing a relatively long-ranged interatomic potential which arises from the nearly free electron model of a metal treated to second order in perturbation theory. The potential exhibits the Friedel oscillations,

$$V(r) = V_0 \frac{\cos 2K_F r}{(2K_F r)^3}, \quad (1)$$

and converges to the interatomic potential derived from second-order perturbation theory at large values of r . Use of the dimensionless quantity $V(r)/V_0$ allows the relative stability of the various phases to be discussed as a function of a single parameter, Z , the valence of the metal. This real space approach to phase stability is easily visualized and, as formulated here, can easily be applied to any close-packed polytype.

The present work also clarifies the distinction between stability against faulting and stability against phase transformation. There exist values of Z for which both the hcp and fcc phases are stable against faulting, but one of the two is unstable against phase transformation. For other values of Z , neither the hcp nor the fcc phase is stable against faulting, and a more complex close-packed phase appears.

c. Microstructures

Kenton L. Hanson and John W. Morris, Jr.

During the past year we inaugurated

research using numerical modeling to simulate simple nucleation and growth transformations in solids. The research addresses two central problems in physical metallurgy: the problem of predicting the microstructure resulting from a given transformation and the converse problem of inferring transformation behavior from the resulting microstructure.

Our initial subject was the microstructure of sections through a body transformed via random nucleation and isotropic growth. The code we employ constructs a cube with periodic boundary conditions, and nucleates grains at random sites within the cube at times determined from a specified probability of nucleation. The grains grow isotropically at a specified rate. The code then plots the microstructures observed on a specified set of plane sections through the cube. The code was written and used to generate hypothetical microstructures under a variety of conditions. The topological properties of these microstructures are under investigation. An intriguing initial observation is the large size variation and irregular, often acicular shapes of the sections of grains resulting from random nucleation and isotropic growth. In conventional metallography these features are often cited as evidence for heterogeneous nucleation sites or preferred growth directions.

2. MECHANICAL PROPERTIES

a. Kinetics of Dislocation Glide

Dale H. Klahn, Kenton L. Hanson, Chol K. Syn, and John W. Morris, Jr.

The mechanical behavior of a crystalline solid is often influenced by dislocation motion through a field of obstacles, for example, forest dislocations, solute atoms, or small precipitates, which are dispersed in a more or less random fashion through the crystal. The problem of predicting the rate of this dislocation motion at finite temperature is formidable. We have been engaged in a detailed study of one of the simplest problems of this type: the thermally activated glide of a dislocation, idealized as a line of constant tension, through a random array of immobile point obstacles under constant applied stress. The study involves theory supplemented by computer simulation of the dislocation glide. Results obtained during the past year include the following.

1) The statistics of thermally activated glide have been brought into a form which

allows the mean and variance of the velocity of glide to be obtained analytically from a properly phrased distribution of the "strengths" of the obstacle configurations encountered by the dislocation as it moves through the array. While this distribution cannot yet be computed analytically, we are now able to predict glide behavior over a wide range of experimental conditions from a single numerical "experiment."

2) In contrast to a frequent assumption, the velocity of glide obeys an equation of the simple Arrhenius form only in the limits of extreme temperature, stress, or obstacle strength. In general the effective activation energy for glide is a function of temperature, stress, and obstacle strength. Its variation with temperature may be related to the "entropy" of the distribution of obstacle strengths encountered as the dislocation glides through the array.

3) Dislocation glide through a random array of obstacles is jerky, as has been observed experimentally. In contrast to frequent assumption, however, the apparent "jerkiness" depends strongly on the temperature as well as the applied stress.

Recently our numerical code has been thoroughly revised. The new form allows easy variation of array size and boundary conditions, and employs a new search algorithm which ensures that any dislocation "looping" will be accurately reproduced. The new code also allows independent variation of the properties of the obstacles; hence arrays of unlike obstacles can be studied. Corollary research on dislocation glide through an array of rod-like precipitates shows that the precipitate field may be regarded as a mixed array of these obstacle types. Force-displacement curves have been derived for these types, allowing numerical simulation of glide through an array of small rod-like particles.

b. Dislocation-Solute Interactions

Chol K. Syn and John W. Morris, Jr.

The edge dislocation-substitutional solute atom interaction in a hexagonal Zn crystal containing a solute addition of Cd or Ag has been estimated and the force-displacement diagram for rigid glide of the dislocation with respect to its solute atmosphere has been computed. Elastic interaction due to both "size" and "modulus" effects was computed; other sources of interaction were neglected. The anisotropy of the dislocation stress field, the lattice distortion by solute atoms, and the elastic

constants of the lattice and solute atoms were incorporated into the calculations. The breakdown of linear elasticity within the dislocation core was artificially removed using a modification parameter suggested by Dorn and Stefansky. The vibrational entropy effect on the configuration of solute atoms along the dislocation line was also taken into consideration.

The following results were obtained.

- 1) The interaction energy contours due to the elastic "size" effect are markedly different in shape from those obtained in the isotropic approximation. The solute-dislocation binding energies due to the "size" effect are much higher (0.81 eV for Ag and 0.39 eV for Cd) than those obtained from isotropic calculations (0.16 eV for Ag and 0.22 eV for Cd).
- 2) When the elastic "modulus" effect is superimposed, the interaction energy contours are slightly perturbed within one Burgers vector of the dislocation core. However, the contours at greater distances are not modified seriously.
- 3) The F-X diagram for Ag and Cd due to elastic interaction contrast strongly. The F-X diagram for Ag has two maxima, while that for Cd has one maximum and is similar in shape to that obtained assuming isotropy.
- 4) Including Dorn-Stefansky core modification lowers the maximum of the F-X diagram by a factor of 20% for Ag and by one order of magnitude for Cd.
- 5) Including the effect of vibrational entropy lowers the maximum by 50% for Cd, but does not sensibly affect the maximum for Ag.

c. High Temperature Creep

Farghalli A. Mohamed, K. Linga Murty and John W. Morris, Jr.

High-temperature creep has been studied in aluminum, lead, and tin in the stress range of 10^{-6} - 10^{-4} GG (is the shear modulus) using double-shear type specimens at temperatures near the melting point. The experimental data reveal that at $\tau < 10^{-5}$ G the dominant creep mechanism changes from climb mechanism to Harper-Dorn creep, a type of viscous deformation reported in pure aluminum and aluminum-3% magnesium at high temperature and low stress. It is characterized by a creep rate which is linearly dependent on the applied stress and apparently independent of grain size. The identifica-

tion of Harper-Dorn behavior in the metals tested was determined from the linear stress exponent, the discrepancy between the experimental values of the creep rate and that obtainable from various mechanisms of viscous deformation, and the close correspondence between the experimental data and the earlier results on aluminum and aluminum-3% magnesium. The experimental results on aluminum reproduce the data of Harper and Dorn almost exactly, despite a significant difference in the sample and load geometries.

The experimental evidence of Harper-Dorn creep in lead and tin along with data indicating the occurrence of the same creep behavior in other materials suggests that Harper-Dorn creep might be a general mechanism for creep at high temperature and low stress. While the details of the process are unknown, available mechanical and microstructural data may be interpreted as due to climb of "saturated" dislocations.

The simple Harper-Dorn creep behavior disappears when the applied stress exceeds a critical value or when sample grain size becomes sufficiently small. In the first case, the rate controlling mechanism changes to climb behavior, while in the second case Nabarro-Herring mechanism dominates.

d. Alloy Design

Sungho Jin and John W. Morris, Jr.

During the past year our effort under this program focused on the development of tough ferritic alloys for use at cryogenic temperatures. This program is conducted jointly with Prof. V. F. Zackay and associates. Accomplishments are reported in the section on High Field Superconductivity.

e. Mechanical Testing Techniques for Use at Cryogenic Temperature

Sungho Jin and John W. Morris, Jr.

Our interest in cryogenic alloys has created a need for simple inexpensive techniques for obtaining good mechanical property data at cryogenic temperature. During the past year a new method of Charpy impact testing at temperatures to 5°K was devised. In this technique a 51 mm Charpy V-notch specimen is wrapped in styrofoam and placed inside a thin-walled lucite box. Liquid helium is then transferred to the box at 2.3 psi dewar pressure and a flow rate of ~ 2 liters/min, using a vacuum-insulated transfer line. A steady-state temperature of 5-6°K is quickly attained and is maintained constant as long as the helium is being

transferred. The measured impact energy is calibrated by subtracting the net energy absorbed by the box, measured to be less than 2 ft lb. Comparison impact tests on boxed and standard samples at liquid nitrogen temperature confirm the accuracy of the values obtained. Tests may be conducted over a range of temperatures by varying the helium pressures and flow rate.

of the results obtained from the numerical experiments.

Research on the dislocation-solute interaction will focus on dislocation break-away through kink nucleation, and on proper computation of the solute atmosphere under near saturation conditions.

3. RESEARCH PLANS FOR CALENDAR YEAR 1973

John W. Morris, Jr.

a. Thermodynamics and Phase Stability

Our principal research emphasis during the coming year will be on the use of pseudo-potential techniques to treat phase stability in alloys. Two approaches to the problem will be investigated. First, using simple model pseudo-potentials it is possible to construct prototype phase diagrams for idealized alloy systems. While the assumptions necessary in this computation preclude a quantitative prediction of the phase diagram of a real alloy, the detailed study of a simple model system should help to clarify the sources of phase stability in real materials of metallurgical interest. Second, given recent advances in pseudo-potential technique, it may now be possible to quantitatively treat dilute solid solutions in simple alloys. Key current problems include proper treatment of the solute size effect and the perturbation due to difference in the valence of the alloy species. We hope to overcome these problems and compute thermodynamic data for the simple alloy systems in reasonable agreement with experiment.

b. Mechanical Properties

Our principal research emphasis during the coming year will continue to be on the theory of dislocation glide through distributions of obstacles. We plan three complementary investigations. First, we hope to complete the theory of thermally activated glide of an idealized dislocation through a random array of like point obstacles by obtaining a theoretical solution for the relevant properties of the obstacle configurations encountered as the dislocation glides through the array. Second, we plan to use the revised numerical code to study more realistic obstacle models, including distributions of obstacle strengths and partially ordered configurations. Third, we plan to resurvey the available experimental data on thermally activated glide in light

4. 1972 PUBLICATIONS AND REPORTS

John W. Morris and Associates

Journals

- *1. J. W. Morris, Jr., The Two-Phase Fluid Interface at Equilibrium: A Continuum Model, *J. Chem. Phys.* **57**, 769 (1972).
2. K. L. Murty, F. L. Mohamed, and J. E. Dorn, Viscous Glide, Dislocation Climb, and Newtonian Viscous Deformation Mechanism of High Temperature Creep in Al-3 Mg, *Acta Met.* **20**, 1009 (1972) (LBL-442).
3. C. Lin, S. Lau, and J. E. Dorn, The Plastic Deformation Behavior of Mo Single Crystals Under Compression, *Phys. Status Solidi A* **11**, 645 (1972).
4. P. G. McCormick and K. L. Murty, On the Effect of Vacancy Sinks and Sources on Serrated Yielding Due to Solute Locking, *Scripta Met.* **6**, 225 (1972) (LBL-194 Rev.).
5. F. A. Mohamed, K. Linga Murty, and J. E. Dorn, On the Kinetics of Ordering in Cu₃Au, *Mat. Sci. Eng.* **9**, 183 (1972) (UCRL-19121 Rev.).
6. K. Linga Murty and J. E. Dorn, On the Non-Equilibrium Factor for Nucleation, *J. Phys. Chem. Solids, Tech. Note*, **33** (3), 757 (1972) (UCRL-20578).

Papers presented

1. D. H. Klahn and J. W. Morris, Jr., Dislocation Glide Through a Random Array of Obstacles, TMS Spring Meeting, Boston, May 1972.
2. C. Liu, J. W. Morris, Jr., and J. E. Dorn, Effect of Re on Anisotropic Slip in Single Mo Crystals, TMS Spring Meeting, Boston, May 1972.
3. K. L. Murty, F. A. Mohamed, J. W. Morris, Jr., and J. E. Dorn, High Temperature Creep Mechanisms in Al-3Mg and Other Metals, TMS Spring Meeting, Boston, May 1972.

4. K. L. Murty, M. L. Vaidya, J. W. Morris, Jr., and J. E. Dorn, Deformation Mechanisms in Superplastic Zn-22Al Eutectoid, TMS Spring Meeting, Boston, May 1972.

5. D. H. Klahn and J. W. Morris, Jr., Characteristic of Dislocation Glide Through a Random Array of Obstacles, John E. Dorn Memorial Symposium, Cleveland, October 1972 (proceedings in press); LBL-1168, November 1972.

6. F. A. Mohamed, K. L. Murty, and J. W. Morris, Jr., Harper-Dorn Creep in Metals at High Temperature, John E. Dorn Memorial Symposium, Cleveland, October 1972 (proceedings in press); LBL-1158, September 1972.

LBL reports

1. D. H. Klahn, Dislocation Modeling of Strain-Rate Phenomena (Ph.D. thesis), LBL-800, March 1972.

2. F. A. Mohamed, High Temperature Creep in Metals at Intermediate and Low Stresses (Ph.D. thesis), LBL-1183, November 1972.

3. C. Liu, J. W. Morris, Jr., and J. E. Dorn, Effect of Rhenium Additions on Anisotropic Slip in Molybdenum Single Crystals, LBL-1148, November 1972 (submitted for publication).

4. M. L. Vaidya, K. L. Murty, and J. E. Dorn, High Temperature Deformation Mechanisms in Superplastic Zn-22Al eutectoid, LBL-459, February 1972.

6. K. E. Amin, K. Linga Murty, and John E. Dorn, Parametrization of Low Temperature Deformation Characteristics in Single Crystals of Molybdenum, J. Appl. Phys., in press (LBL-407 Rev.).

7. J. W. Morris, Jr., and P. L. de Bruyn, The Two-Phase Interface in a Simple One-Component Fluid, J. Colloid Interface Sci., in press (LBL-454).

8. F. A. Mohamed, K. L. Murty, and J. W. Morris, Jr., Harper-Dorn Creep in Al, Pb, and Sn, Met. Trans., in press (LBL-831, May 1972).

C. RELATION OF MICROSTRUCTURE AND PROPERTIES

Gareth Thomas, Principal Investigator

Introduction. One of the objectives of research relating structure and properties is to be able to design economically, alloys with desirable structures for particular applications and properties. Over the past eight years we have been concerned with two such examples:

- a) the control of transformation sub-structure in martensite and bainites in structural steels leading to strong, tough economical steels
- b) the development of high strength dispersion strengthened systems without involving plastic deformation.

These programs have involved detailed and systematic studies of a series of alloys by quantitative electron microscopy.

Success has been obtained in both these areas; in a) it has been shown that toughness can be achieved in relatively high carbon steels (~ 0.25% C) provided twinned martensite and inter-martensite or bainite carbide films are avoided. In b) the martensite transformation is utilized to produce dislocation-particle interactions and thus dispersion strengthening in prior dispersed austenite. The latter is achieved by, e.g., aging or spinodal transformation.

Work is continuing in understanding phase transformations from a fundamental view point, e.g., studies of martensite nucleation in single crystals, bainitic transformations, spinodal and ordering transitions.

The abstracts following are representative of the current programs.

1. STRUCTURE, STRENGTH AND TOUGHNESS OF Fe-Cr-C MARTENSITIC STEELS*

John A. McMahon and Gareth Thomas

This research is part of a continuing program involving a systematic study of the composition dependence of martensitic structure as revealed by electron microscopy (dislocated or twinned, carbide type, and morphology) and its relation to strength and toughness. The overall objective is the improvement in design of structural steels by simplifying composition and heat treatment to minimize costs.

Fig. 1. Typical as-quenched microstructures of 0.35 wt% C alloys. Alloy 0435 contains a mixed structure of dislocated laths (a) and twinned plates (b). Alloy 1235 also has a mixed structure, shown in (c) and (d), although the twin density in this alloy is much higher than that of alloy 0435.

(XBB 7211-5622)

In the Fe-Cr-C steels studied (4-12 wt% Cr; 0.16-0.35 wt% C), the as-quenched martensitic structure as well as carbide morphologies produced by tempering at 200, 400, and 600°C were correlated with tensile and fracture (K_{IC}) properties. In this paper we present new results concerning the strength and toughness of the untempered martensites. For a given carbon level, the volume fraction of martensite containing twins increased with chromium concentration, demonstrating that chromium induces transformation twinning in martensite (Fig. 1). Ms temperature measurements showed that increasing the chromium content also lowers the Ms temperature.

The mechanical properties of the as-quenched and tempered structures were determined by using tensile, compressive, and plane strain fracture toughness tests. It

Fig. 2. Yield strength versus fracture toughness for all alloys under various tempering conditions, giving a strength/toughness comparison of dislocated and twinned martensites. (XBL 7211-7159)

Fig. 3. Comparison of ultimate tensile strength and fracture toughness of alloy Q435 with the strength/toughness properties of several ultra-high-strength commercial steels. (XBL 7211-7161)

was found that for the same carbon level, an increase in the amount of transformation twinning due to an increased chromium concentration has a dramatic and deleterious effect on the fracture toughness of the as-quenched steels. In two of the steels con-

taining 0.35 wt% carbon, raising the chromium content from 4 to 12 wt% caused the percentage of twinned martensite to increase from approximately 20% to greater than 30% (as estimated from electron micrographs), and the plane strain fracture toughness to drop from 75 to 25 $KSI\sqrt{IN}$. The high chromium alloy also had a higher yield strength: 300 ksi vs 240 ksi for the low chromium alloy. However, when tempered to an equivalent yield strength, the 12 wt% chromium alloy with a high twin density continued to have much poorer fracture toughness compared to the 4 wt% chromium alloy with a lower twin density (see Fig. 2). Thus it has been established that with the carbon content held constant, there is a direct correlation between the transformation twin density, chromium content (and Ms), and strength and toughness in Fe-Cr-C steels.

One of the results of this systematic study of the microstructure and mechanical properties of Fe-Cr-C steels has been the discovery of an alloy with mechanical properties comparable to those of 18 Ni maraging steels (Fig. 3) and which could be produced at a significantly lower cost.

We appreciate the continued support of Dr. Frank Hultgren, Republic Steel Corporation, who kindly provided all the alloys.

* Based on LBL-1181 (J. A. McMahon, M.S. thesis).

2. MARTENSITIC TRANSFORMATION AND STRENGTHENING OF A SPINODAL Fe/Ni/Cu ALLOY*

Gareth Thomas and C. Vercaemer†

A 61 at.%Fe/20 at.%Ni/19 at.%Cu alloy has been designed which can be subsequently transformed to martensite following spinodal heat treatment (aging at 850°C). Morphological changes were followed by transmission electron microscopy Figs. 1 and 2. Ms temperatures were estimated by an electrical resistivity technique and changes in microhardness were measured. The Ms temperatures increased rapidly, then were unchanged as particle coarsening started and wavelength λ increased. The hardness first increased rapidly, then age-softened as λ increased.

Although the specimens were brittle, the considerable increases in hardness achieved by martensitic transformation compared to the hardness of purely spinodal

Fig. 1. Transmission electron micrographs in bright field. (a) As quenched: $\lambda \sim 360\text{\AA}$, and aged at 850°C for (b) 3 min, $\lambda \sim 205\text{\AA}$; (c) 9 min, $\lambda \sim 360\text{\AA}$; (d) 2 hr, $\lambda \sim 890\text{\AA}$.
(XBB 7112-5991)

Fig. 2. Transmission electron micrographs showing martensite in the 70 hr aged alloy; (a) bright field, (b) dark field of austenite spot reversing contrast. M represents the martensitic area and A the austenitic area.
(XBB 7112-5993)

Fig. 3. Variation of hardness with aging time for samples quenched in water and in liquid nitrogen. Aging temperature 850°C. Livak and Thomas' results have been represented for comparison (aged at 625°C compared to 850°C in the present alloy).

(XBL 7112-2204)

alloys (Fig. 3) indicates that this double phase transformation method may be promising for improving the strength, and could replace ausforming in certain alloys.

* LBL-447, Met. Trans., 3, pp 2501-2506 (1972).

† Now returned to Département Science des Matériaux, Université de Strasbourg, France.

3. THE TEMPERING OF MARTENSITE IN AN IRON 1.5% NITROGEN

R. D. Garwood[†] and Gareth Thomas

The tempering of iron-1.5% nitrogen martensite has been studied at temperatures up to 300°C, using X-ray and electron microscope techniques. Stage 1 decomposition occurs below 270°C by the general precipitation, resembling spinodal morphology, of fine α'' (Fe_{16}N_2) lamellae on {001} habit planes in both matrix and twin crystals of the partially [112] twinned martensite plates (Fig. 1). Yet, gauged by changes in the X-ray spectrum, the reaction is discontinuous, the tetragonal martensite doublets decaying in intensity without change in their Bragg positions (Fig. 2). The anomaly and the failure to detect by electron microscopy regions exhibiting fractional stages of the fine scale $\alpha' + \alpha + \alpha''$ reaction is attributed to its occurrence at different times in different martensite (or parts of martensite)

Fig. 1. Dark field electron micrographs of [112] type twinned iron-1.5% nitrogen martensite tempered 1 hr at 200°C showing α' lamellae on {001} α habit planes in both parent (a) and twin (b) lattices. In (a) the operating reflections are the combined $(110)\alpha + (220)\alpha'$ parent spots and in (b) the $(002)\alpha'$ in the twin. The α'' lamellae in the parent crystal are less distinct in (a) because of their smaller inclination to the foil plane (650 kV). The diffraction pattern (schematic) is shown in (c) while (d) is a stereographic analysis of the twin and α' lamellae traces (650 kV). (XBB 722-1254)

plates. It is believed that transformation occurs in this manner because the nucleation of coherent α'' plates is controlled by the prevailing internal stress field. Thus the time exponent 'n' for the reaction decays from a normal value between 1 and 0.67 to less than 0.3 as stress relief by recovery dominates the more protracted stages of the reaction.

Above 200°C the more stable nitride γ' (Fe_4N) forms at an increasing rate as plates

Fig. 2. Changes in the X-ray spectrum in the region of the (101)-(011)_h martensite doublets on tempering an iron-1.5% nitrogen alloy at 150°C for the times indicated. Cobalt K_{α} radiation. (XBL 727-6600)

Fig. 1. Plot of stress intensity to initiate crack propagation and yield stress vs. (grain diameter)^{-1/2}, showing the linear dependence of these two parameters on $d^{-1/2}$. (XBL 717-7014)

on {012} habit planes, accompanied by marked softening.

* LBL-470, Met. Trans. in press

† Department of Metallurgy, University College, Cardiff, Great Britain.

4. INTERGRANULAR FRACTURE OF AGED Cu-Ni-Fe ALLOYS*

Ronald J. Livak† and William W. Gerberich‡

Cu-Ni-Fe alloys are subject to intergranular cracking as a result of preferential coarsening of particles near the grain boundary and also because of the discontinuous precipitation reaction which occurs. Figure 1 shows the linear dependence of the observed yield stresses and stress intensities on grain size, which obeys the relation:

$$K_{\text{nucl.}} = (\phi/d)^{1/2} \epsilon^* \lambda E$$

where ϕ is a constant, d is the grain diameter, ϵ^* is fracture strain at the grain boundary, λ is the width of the grain boundary region, E is Young's modulus.

This relationship is explained in terms of the microstructural differences between the grain boundary regions and the matrix which results in the development of a triaxial stress state at the boundaries during deformation. The problem is analogous to that with brazed joints. Although Cu-Ni-Fe alloys are relatively ductile, failure occurs preferentially at grain boundaries, because of the softer material there.

* Electron Microscopy and Structure of Materials, edited by G. Thomas (U.C. Press, 1972).

† Part of Ph.D. thesis (LBL-1107) of R. J. Livak, now at Bell Telephone Research Labs., N.J.

‡ Now at University of Minnesota.

5. SHORT RANGE ORDER IN Ni-Mo, Au-Cr, Au-V, AND Au-Mn ALLOYS*

Santosh K. Das,† P. R. Okamoto,†
P. M. J. Fisher‡ and Gareth Thomas

The nature of short range order (sro) has been investigated in the systems Au₄Cr, Au₃Cr, Ni₄Mo, Ni₃Mo, Au₃Mn, and Au₄V by transmission electron microscopy and diffraction. The

Fig. 1. (a) [001] reciprocal lattice section containing D1a, Ni₂Mo, {1 1/2 0} sro spots; (b) [130] reciprocal lattice section. (XBL 717-7009)

Fig. 2. (a) [001] diffraction pattern of evaporated thin film of Au₃Mn showing two-dimensional long period superstructure (Watanabe type), (b) another [001] pattern showing additional D1a superlattice spots, (c) sketch of [001] pattern corresponding to Watanabe-type structure. (XBB 717-3414A)

examination of the sro state, at temperatures above the critical temperature (T_c) for order-disorder transformation and also in the samples that were quenched from above T_c , showed diffuse scattering peaks centered near {1 1/2 0} positions in the fcc reciprocal lattice, whose shape changed from one system to another. Evidence for diffuse scattering near superlattice positions corresponding to the D1a structure was obtained in the sro state of Au-Cr, Au-V, and Ni-Mo alloys. Additional diffuse scattering was observed near Ni₂Mo positions in the Ni-Mo alloys. Figure 1 shows schematically the diffraction patterns that are observed. The diffraction patterns of Au₃Mn above T_c showed evidence for diffuse scattering near the superlattice positions corresponding to Watanabe type two-dimensional long period superstructure (e.g., Fig. 2).

Using the pairwise interaction parameters up to third nearest neighbors in the existing statistical thermodynamic model of Clapp and Moss, one can partially account for the shapes of {1 1/2 0} sro spots in Ni-Mo and Au-Mn alloys, but not in Au-Cr and Au-V alloys. On the other hand the diffuse sro scattering in all these alloys can be qualitatively explained by assuming the presence of imperfectly ordered microdomains or various superstructures that may exist in the long range ordered (lro) state in these alloys. For a particular stoichiometry the structures of the microdomains that exist above T_c may or may not correspond to the equilibrium lro structure obtained at that stoichiometric composition.

* LBL-441, Acta Met., in press.

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D. HIGH VOLTAGE ELECTRON MICROSCOPY

Gareth Thomas, Principal Investigator

Introduction. High voltage electron microscopy has advantages in improved penetration and resolution and can be used to study directly knock-on damage in inorganic crystals. With increasing energy there is a limit to the useful thickness which can be penetrated if high resolution information is to be obtained. This appears to be ~ 1 MeV for most materials except very light elements. On the other hand, increasing the energy of the electron beam reduces damage from inelastic and elastic scattering processes (e.g., ionization damage). It appears therefore that very high energies may be beneficial for research on beam-sensitive materials (polymers, biological bodies). At the present time there are only two microscopes in the world (Toulouse, France and Osaka, Japan) which have capabilities up to 3 MeV. However, in collaboration with Prof. R. M. Glaeser (Medical Physics) we intend to make an in-depth study of the potential of HVEM up to, say, 5 MeV. It should be noted that it may not be possible to produce stable beams above 3 MeV (and two parts in 10^6 volts is necessary for instrumental resolution $\sim 5\text{\AA}$ or better), so that any gain in specimen lifetime from reduced specimen damage may be offset by poorer resolution. The costs for a 3-5 MeV microscope would be very very high.

In inorganic materials an up-to-date survey of the current status of the theory and applications of HVEM is given in the Proceedings of our 1971 IMRD Conference, *Electron Microscopy and Structure of Materials*, published by the University of California Press, 1972.

Following are examples of current work in which emphasis is being placed upon improved resolution and penetration, enabling us to develop more structure-property programs on non-metallic systems.

1. TRANSMISSION ELECTRON MICROSCOPY AT 2.5 MeV*

Gareth Thomas and J. C. Lacaze†

Measurements of electron penetration on silicon and austenite stainless steels have been continued, using the same criteria as established previously [G. Thomas, Phil. Mag. 17, 1097 (1968)]. The work was done up to 2.5 MeV, using the 3 MeV Toulouse microscope.

Fig. 1. Penetration data obtained for silicon and stainless steel. Open circles correspond to thicknesses for which up to six fringes are visible at stacking faults. Closed triangles correspond to total loss of fringes. The open triangle at 2.5 MeV corresponds to the thickness for which all fringes are just visible. (XBL 728-6771)

The data are shown in Fig. 1, from which it is seen that for silicon the penetration increases up to about 14μ , whereas for steel little or no gain is apparent. Primary knock-on damage occurred readily in both materials.

The critical voltages for the 440 reflection in silicon and 422 in tantalum were measured. Both were found to be $1.4\text{ MeV} (\pm 10\text{ kV})$.

Measurements of radiation damage in valine and glycine by observing the disappearance of single-crystal spot diffraction patterns as a function of beam current and voltage showed that the critical exposures for complete fading of the patterns increased with increasing voltages. Due to difficulties in measurements of the current and end-point determinations, the magnitude of the increase is not yet known with much accuracy. Work is continuing on this problem, and at Berkeley we plan to study lifetimes of these materials by exposure to 5-15 MeV beams in Linacs, followed by examination in our 650 kV microscope.

* LBL-1119(Rev); J. Microscopy, in press;
G. T. acknowledges support from a Guggenheim Fellowship.

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2. DEFECT CONTRAST AND RESOLUTION IN HIGH VOLTAGE ELECTRON MICROSCOPY*

M. J. Goringe,† E. A. Hewat,† C. J. Humphreys† and Gareth Thomas

The importance of several non-conventional techniques in transmission electron microscopy for the improved imaging of defects has already been recognized. Significant benefits of improved imaging of dislocation lines and quantitative applications to problems of dislocation structure and stacking fault energy measurements have been demonstrated at 100 kV by the dark-field weak-beam technique (e.g., Cockayne et al., 1969). Comparably narrow dislocation images have been produced by high voltage electron microscopy, using bright-field images when the crystal is oriented near high order systematic reflections.¹⁻³ Reasonably narrow, high contrast images have been produced in the second-order dark-field image when the accelerating voltage is the critical voltage.^{3,4} The present program of research is aimed at evaluating the advantages and disadvantages of these various techniques and to determine their fields of application for the quantitative characterisation of defects in solids.

Fig. 2. Dissociated edge dislocation profiles. (14 1/2, 14 1/2, 0) satisfied. 000, 220, and 220 (dotted) images. Case for Cu. 1000 kV, $t = 1634\text{\AA}$ at depth 817\AA, $g.b = 1$ for both partials. (XBL 731-5648)

At 100 kV, dislocation images may normally be understood by using two-beam theory which considers the two most strongly excited dispersion surface branches. As is well known, the image width is then about $\xi_g/3$ where ξ_g is the extinction distance [$\xi_g = (\Delta k)^{-1}$, where Δk is the separation of the two branches]. At higher voltages many-beam interactions become more important, and for an understanding of defect contrast a larger number of dispersion surface branches must normally be considered. Figure 1 illustrates the situation for a crystal oriented near the third-order Bragg reflecting position. At A the third order is exactly satisfied. For the bright-field image, at 100 kV the transition 3 - 4 is the only one

Fig. 1. Schematic dispersion surfaces illustrating important interband transitions caused by dislocation. A is for $3g$, $s = 0$. B is $3g$, $s > 0$. (XBL 731-5647)

Fig. 3. Deformed Si showing dissociated and decorated dislocation imaged 100 kV B.F. ($0,4g$) $s > 0$ ($g = 220$). (XBB 731-265)

Fig. 4. Cu, edge dislocation. 222 satisfied. $b = 1/2[110]$ (a) 470 kV; (b) 386 kV = V_C ; (c) 300 kV. Thickness = $5.5\xi_g$, dislocation depth = $3\xi_g$. [Notation: (g,ng) means image formed in beam g with ng satisfied.]

(XBL 731-5649)

of importance, but at 1 MV all the transitions indicated are important, because more Bloch waves are appreciably excited and more inter-band transition probabilities are large. Since different interactions can give rise to images in different positions, a complicated image may result. Note however that at the critical voltage the image is simplified. In particular, image tails due to 2 - 3 transitions will be absent. At B (positive of third-order Bragg position) the situation is less complicated but still involves at best two interactions for the bright field image. For the first-order

dark-field image, such as used for weak-beam work, a single transition (2 - 4) is dominant. Similar reasoning applies to any order reflection along the systematic row, the Δk value of the dominant transition increasing with increasing order. The implications for microscopy are that both high-order bright-field and weak-beam images may be narrow--see Fig. 2 (because of the large Δk values, and hence small ξ_g value, involved), but the bright-field image may be more complicated for quantitative analysis (two interactions rather than one), unless very high order reflections are used.

Micrographs and computed profiles for specific cases are shown in Figs. 2-4. Points to note are the narrowing of both bright- and dark-field images with increasing order. In the bright-field case the limit to the order is set by lack of contrast. Very small image width is shown by the dissociated dislocation of Fig. 3 (image peak separation 90Å). Note also the decoration effects after electron irradiation in the beam. The image profiles of Fig. 4 illustrate the improvements of the image at the critical voltage, both in terms of simpler image and higher contrast due to the low background.

* LBL-841; Proc. EMCON 1972, Inst. of Physics (London), 1972, p. 538. Financial support is acknowledged from SRC and the Guggenheim Foundation (G.T.)

† Department of Metallurgy, University of Oxford, Oxford, England.

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3. HIGH VOLTAGE ELECTRON MICROSCOPIC STUDIES OF MINERALS*

Wolfgang F. Muller, H.-R. Wenk,† and Gareth Thomas

a. On the Transformation Ortho-enstatite to Clino-enstatite

The ortho-clino inversion in enstatite ($MgSiO_3$) is interesting because the trans-

Fig. 1. High voltage electron microscopy of undeformed and deformed Bamble enstatite. Left: BF electron micrograph of an undeformed specimen showing ortho-enstatite with stacking faults parallel to (100). Center: BF electron micrograph of the deformed specimen showing alternating lamellae parallel to (100) of untwinned clino-enstatite and ortho-enstatite. Right: Selected area electron diffraction pattern corresponding to the micrograph in center showing the relation of the ortho- and clino-enstatite reciprocal axes to each other and to the compression directions (heavy arrows). 650 kV acceleration voltage. (XBB 727-3691)

formation from the orthorhombic to the monoclinic polymorph is dramatically promoted by shearing on (100) planes parallel to [001], but is only slightly promoted by hydrostatic compression. Earlier investigators found that clino-enstatite (CE) formed during deformation has the $[a]$ and $[b]$ crystallographic axes in common with the parent ortho-enstatite (OE) and has (100) as habit plane. But they could not deduce the position of the $[c]$ axis uniquely. The electron microscope study was done on a sample from a Bamble-enstatite specimen shortened 3.7% at a strain rate of 10^{-4} sec^{-1} with a confining pressure of 5 kbar and a temperature of 800°C. This sample was provided by Prof. R. Coe, U.C. Santa Cruz. The preparation method, i.e., ion-thinning of a pre-selected area, enabled correlation to be made of the electron micrographs and diffraction patterns to the oriented petrographic thin section, so that the compression direction of the deformation experiment is known on the micrographs. Electron microscopy revealed submicroscopic lamellae which are alternately OE and untwinned CE in contact, on (100) habit planes and with axes a and b parallel ($|b_{OE}| = |b_{CE}|$, $|a_{OE}| = 2|a_{CE}|$). Figure 1 displays electron micrographs of undeformed enstatite [containing stacking faults parallel to (100) in some areas] and of the deformed enstatite; the orientation of the c axis of CE with respect to the compression direction is shown in the diffraction pattern. It is the orientation made likely by the optical measurements of Trommsdorff and

Wenk (1968) and favored in the mechanism of Coe (1970). It contradicts the transformation mechanisms suggested by Turner et al. (1960), Brown et al. (1961) and Starkey (1968).

* Joint program with Geology.

† Associate Professor, Geology.

b. Order in Anorthite*

Calcic plagioclase feldspars with a chemical composition ranging from $\text{Ca}_{0.9}\text{Na}_{0.1}\text{Al}_{1.9}\text{Si}_{2.1}\text{O}_8$ (An 90) to $\text{CaAl}_2\text{Si}_2\text{O}_8$ (An 100) are called anorthites. Two different types of APBs may occur: Type b APBs (imaged with b-reflections: $h + k$ odd, l odd; first observed by Christie et al., 1970) and type c APBs (imaged with c-reflections: $h + k$ even, l odd). Presence and size of antiphase domains depend on the chemical composition and the cooling history of the anorthite. A comparative study of terrestrial, meteoritic, and lunar anorthites with the high voltage microscope showed that the size of domains increases with increasing An-contents in the slowly cooled metamorphic and plutonic rocks. Type c domains were small or not resolvable in volcanic, i.e., quenched, rocks (compare electron micrographs f and g in Fig. 2; the chemical composition is the same in the volcanic and meteoritic anorthite).

Type b-APBs were absent in all terrestrial anorthites studied so far which had chemical compositions ranging from An 94 to An 100. They were present, however, in the calcic plagioclase (about An 85 to An 95) from lunar basalt 14310 (Fig. 2, first line). Most of the b-APBs were 500 to 1000 Å wide, but in rare cases larger b-domains have been observed in the same specimen. No c-domains have been resolved in anorthites from 14310.

The antiphase vector of c-APBs was analyzed as $1/2 [a + b + c]$. Figure 3 shows c-APBs in anorthite from Val Pasmada, S. Tyrol (An 100). The fringes have the properties expected for the phase factor $\alpha = \pi$, thereby providing additional proof for the antiphase vector $1/2 [a + b + c]$. Calculated intensity profiles applying multi-beam dynamical theory are in agreement with the observed fringe patterns.

* Mineralogy and Petrology 34, 304-314 (1972). (LBL-460).

Fig. 2. Structural variations in anorthites. 1st line: lunar basalt 14310; 2nd line: volcanic tuff, Japan; 3rd line: meteorite Serra de Magé; 4th line: metamorphic calcisilicate rock, Alps. The electron micrographs are dark field images taken at 650 kV acceleration voltage. (XBB 7112-6108)

Fig. 3. Type c APBs in anorthite from S. Tyrol in bright and dark field. 650 kV acceleration voltage. (XBB 728-4151)

4. HIGH ANGLE TILTING STAGE FOR THE 650 kV HITACHI MICROSCOPE*

Marcel Bouchard, William L. Worthington,
Donald J. Jurica, and P. R. Swann†

A new tilting stage has been developed which allows $\pm 30^\circ$ tilt in any direction. This stage does not require any modifications to the microscope. Figure 1 shows the diagram of the new stage.

* LBL-1145; Rev. Sci. Instr., in press.

† Reader in Metallurgy, Imperial College, London, England.

Fig. 1. a) Schematic cross section of the tilting stage.

b) Magnified portion of the tilting mechanism showing the sphere in the zero (0°) tilt position.

c) Magnified portion of the tilting mechanism showing the sphere in the maximum (30°) tilt position. (XBL 728-6878)

5. LITHIUM FERRITE

Omer Van der Biest

Work is progressing on characterizing the structure of LiFeO_8 in which studies are being made of the order-disorder transition. Anti-phase domain boundaries with $\vec{p} = a/2 \langle 110 \rangle$ have been identified by con-

trast experiments. Stacking faults on $\{110\}$ have been found in the cation sublattice and also (and unexpectedly) $\{111\}$ faults on the oxygen sublattice.

Dislocations in lithium ferrite are dissociated into two partials of Burgers vectors $a/4 \langle 110 \rangle$. These define a stacking fault in the cation sublattice.

Present work is concentrated on a more quantitative analysis of the defect structures and precipitation reactions including studies of the interphase interfaces.

6. OTHER RESEARCH PROJECTS IN PROGRESS

Gareth Thomas

a) Phase Transformations

(i) Bainitic transformations in a range of steels have been studied. The results indicate that there is no sharp transition between upper and lower bainite. Epsilon carbide has been identified in lower bainite; bainite can also contain transformation twins, i.e., bainites can have the same range of structural features as tempered martensites.

(ii) Structure and mechanical properties have been studied in Cu-Mn-Al alloys some of which undergo order + spinodal reactions. These alloys are useful in magnetic applications but are mechanically brittle.

(iii) Transformations in ceramics and minerals. Studies of order-disorder in lithium ferrite show existence of LRO with $a/2 \langle 110 \rangle$ a.p.b.s. In addition, faulting has been resolved both in the anion and cation sublattices. Order has also been investigated in anorthites and two different types of a.p.b. have been detected in both terrestrial and lunar samples.

b) Contrast and Resolution in HVEM

Unconventional techniques such as high order bright field imaging or weak beam dark field imaging in systematic reflections have been shown to improve lattice defect resolution considerably. Work is being done to resolve closely spaced dislocation pairs and, in a cooperative program with Professor J. Washburn, to interpret contrast from defects in ion-implanted silicon.

c) Martensite Formation in Single Crystals

Mechanism of strain-induced transformations and mechanical properties of metastable

austenitic stainless steels are being investigated in single crystals of various orientations so as to obtain single and multiple slip systems in austenite.

7. RESEARCH PLANS FOR CALENDAR YEAR 1973

Gareth Thomas

a. Alloy Strengthening

Continuation of program on Fe-Cr-C and Fe-Mo-C steels with emphasis on improving strength and toughness. Program will include studies of lower bainites corresponding to those alloys which are brittle in the martensitic state.

Work will be expanded to cover a wider range of alloys in the Cu-Mn-Al system so as to better understand the phase relationships and properties. Further studies on spinodal Fe-Ni-Cu will be done in an effort to prevent the grain boundary reaction and embrittlement.

b. Non-metals

Work on mineralogy will be slower due to the departure of W. F. Miller, but we hope for extra funding from NSF to keep the joint program with Professor Wenk (Geology) going.

Current work on spinels will be continued. Searches will be done for spinodal systems. Studies of plastic deformation and phase transformations in minerals (joint program with Prof. Wenk, Geology) will be continued.

c. New Projects

New projects under way on a joint program with Prof. R. M. Glaeser (Medical Physics) include studies of high energy electron irradiation damage in organic/biological materials, e.g., Linac work on amino acids (5-15 MeV), viruses, etc., and evaluation of the potential of 5-10 MeV electron microscopy.

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Gareth Thomas and Associates

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E. ALLOY DESIGN

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Principal Investigators

INTRODUCTION

The application of the first principles of materials science to develop new and improved alloys is a relatively recent approach to the problem of alloy design. Virtually all of the presently available commercial alloys have been discovered by trial-and-error methods. This approach is no longer feasible because of its inefficiency and expense. Further, such an approach is totally inadequate to meet the complexity of material requirements of present and future technology.

Mechanical properties of alloys largely depend on chemical composition and structural features such as crystal structure, defect structure, and microstructure. The development of a unified theory of fracture toughness has done much to relate quantitatively the variables of chemical composition and microstructure to fracture toughness. The high resolution instruments needed to analyze composition on a microstructural scale and to characterize elements of structure whose dimensions are of the order of a micron or a fraction of a micron are now readily available. It is our belief that the availability of these instruments coupled with an understanding of the principles of dislocation theory, thermodynamics, alloy chemistry, and micromechanics of deformation and fracture will aid in the development of superior alloys. Examples of present efforts directed toward this goal include the following:

- 1) Study of these chemical and microstructural features which control the mechanical properties of low alloy ultra-high strength steels.
- 2) The design, from first principles, of an interstitial-free cryogenic alloy.
- 3) The design and development of a non-carbon-containing precipitation hardening ferritic alloy for elevated temperature applications.
- 4) The design of new TRIP steel processes which involve a minimum of prior austenite deformation.
- 5) The design of high manganese-high carbon steels utilizing a strain induced transformation.

Concurrent with the studies mentioned above has been the development of a rapid magnetometric technique for detecting the early stages of isothermal transformations in steels.

1. THE FRACTURE TOUGHNESS OF ULTRA-HIGH STRENGTH ALLOY STEELS

William E. Wood

This investigation showed that the toughness of several commercial low alloy high strength steels is a sensitive function of their microstructure and heat treatment. It was also concluded that the commonly used Charpy-V-notch test is not sensitive to small changes in microstructure which can drastically alter fracture toughness.

The steels used in this study were AISI 4130, 4330, 4340, 4140, and 300-M. Their compositions are listed in Table I. The normal commercial heat treatment for all the above steels consists of austenitizing for 1 hr at 870°C followed by oil quenching. However, austenitizing at temperatures up to 1200°C (and for some steels by quenching into solutions as severe as ice brine) followed by refrigeration in liquid nitrogen, a drastic change was observed in the fracture toughness.

Figure 1 shows the room temperature plane strain fracture toughness of AISI 4130 as a function of tempering temperature for both the commercial heat treatment and the 1200°C austenitizing treatment followed by an ice brine quench and liquid nitrogen refrigeration (LBQLN). An increase in fracture toughness of 100% was observed for the latter treatment over the former. This increase was associated with a microstructural change from a mixed microstructure of blocky ferrite and

Fig. 1. The effect of tempering temperature on the room temperature plane strain fracture toughness, K_{IC} , of AISI 4130, austenitized and quenched as indicated. (XBL 731-5651)

Table 1. Chemical compositions of steels.

Steel type	C	Mn	Cr	Ni	Mo	S	Si	V
AISI 4130	0.30	0.46	0.85	0.15	0.20	0.011	0.28	
AISI 4330	0.30	1.02	0.85	1.80	.40	.007	.28	0.05
AISI 4340	0.41	0.80	0.72	1.70	.24	.011	.23	
300-M	0.40	0.79	0.75	1.85	.43	.003	1.50	0.09

Fig. 2. Microstructure of AISI 4130, oil quenched from the austenitizing temperature of 870°C, showing blocky ferrite and martensite. (XBB 731-377)

martensite, Fig. 2, to one that was completely martensitic, Fig. 3. As seen from Fig. 1, a heat treatment of 1200°C followed by an oil quench resulted in an intermediate level of fracture toughness. The microstructure associated with this heat treatment was mostly martensite but with regions of upper bainite along prior austenite grain boundaries. (See Fig. 4).

The steel AISI 4330 was similar to 4130 in that the best results were attained by

using the same heat treatment, Fig. 5. However, most notable was the observation that 4330 did not exhibit temper embrittlement at tempering temperature above 200°C. The absence of temper embrittlement was believed to be due to the presence of a small amount of vanadium, which prevents the formation of carbide films. Scanning electron fractographs of embrittled 4130 tempered for 1 hr at 350°C after an ice brine quench from 1200°C are shown in Fig. 6. The scanning electron fractograph for non-embrittled 4330 with the same heat treatment is shown in Fig. 7.

Fig. 3. Microstructure of AISI 4130, ice brine quenched from the austenitizing temperature of 1200°C. The structure is almost completely martensitic. (XBB 731-374)

Fig. 4. Microstructure of AISI 4130, oil quenched from the austenitizing temperature of 1200°C, showing upper bainite at the prior austenite grain boundaries, and martensite. (XBB 731-375)

Fig. 6. Scanning electron fractograph of AISI 4130, austenitized at 1200°C for 1 hr, ice brine quenched, refrigerated in liquid nitrogen, and tempered at 350°C for 1 hr, and tested for K_{IC} at room temperature. Fracture occurred by intergranular cleavage. (XBB 731-376)

Fig. 5. The effect of tempering temperature on the room temperature plane strain fracture toughness, K_{IC} , of AISI 4330, austenitized and quenched as indicated. (XBL 731-5652)

Whereas the 4330 had a very ductile fracture mode, the 4130 exhibited an intergranular cleavage mode of failure.

The higher carbon steels also showed a marked improvement in toughness although the optimum properties could be achieved with an oil quench. The 300-M steel was similar to 4330 in that it did not embrittle. The plane strain fracture toughness increased when the tempering temperature was raised, as shown in Fig. 8. Finally, steel 4340 which did not have any vanadium did exhibit an embrittlement on tempering at temperatures above 300°C, as indicated by the variation of plane strain fracture toughness with tempering temperature (Fig. 9). In the case of 4340 a straight quench from 1200°C caused quench cracks; therefore, the steel was quenched first to 870°C and then into oil. A result that was common to all the steels was the increase in grain size from ASTM 7-8 to 0-1 when the austenitizing temperature was raised from 870 to 1200°C.

Fig. 7. Scanning electron fractograph of AISI 4330, austenitized at 1200°C for 1 hr, ice brine quenched, refrigerated in liquid nitrogen, and tempered at 350°C for 1 hr, and tested for K_{IC} at room temperature. The mode of failure was dimpled rupture.

(XBB 731-373)

Fig. 8. The effect of tempering temperature on the room temperature plane strain fracture toughness, K_{IC} , of the 300-M steel, austenitized and quenched as indicated.

(XBL 731-5653)

Fig. 9. The effect of tempering temperature on the room temperature plane strain fracture toughness, K_{IC} , of AISI 4340, austenitized and quenched as indicated.

(XBL 731-5654)

Finally impurity elements and inclusions are well-known sources of poor toughness. Investigations are in progress to determine the role of both the amount and distribution of impurity elements and inclusions on the fracture toughness of AISI 4340.

2. STRUCTURE AND FRACTURE TOUGHNESS OF SECONDARY HARDENING STEELS

Thomas Tom

The relation between microstructure and fracture toughness was studied in several secondary hardening steels of varying carbon, molybdenum, and nickel contents. The austenitizing temperature, the tempering temperature, and the chemical composition were found to have a considerable influence on the plane strain fracture toughness, K_{IC} , by virtue of their role in changing microstructure.

The nominal compositions of the steels are listed in Table I. The heat treatment consisted of an hour austenitizing treatment at several temperatures from 1600 to 2200°F followed by ice brine quenching and refrigeration in liquid nitrogen to insure complete transformation to martensite. One hour tempering treatments at 400 and 575°F were investigated for the 2200°F austenitizing treatment.

The room temperature plain strain fracture toughnesses of steels A and C are plotted in Fig. 1 as a function of the austenitizing temperature. The K_{IC} value increased considerably when the austenitizing temperature was raised to 2000°F and above. The higher K_{IC} for the higher austenitizing temperatures were attributed to the elimination of undissolved carbides, a more favorable distribution of impurities such as sulphur and phosphorous, and to auto-tempering (depletion of carbon from solution).

Fig. 1. Influence of austenitizing temperature on the room temperature plane strain fracture toughness of secondary hardening steels A and C tested in the as-quenched condition. (XBL 731-5623)

Table I. Chemical compositions of steels.

Designations	Compositions, wt%			
	C	Mo	Ni	Mn
A	0.3	5	--	0.6
B	0.4	5	--	0.6
C	0.3	4	3	0.6
D	0.4	4	3	0.6

Fig. 2. Fractographs of steel A austenitized at (a) 1600°F and (b) 2200°F, ice brine quenched and tested at room temperature for plane strain fracture toughness. (XBB 731-372)

Fig. 3. Influence of austenitizing temperature on the room temperature fracture toughness of secondary hardening steels B and D tested in the as-quenched condition. (XBL 731-5624)

Scanning electron fractographs of specimens of steel A austenitized at 1600 and 2200°F indicated a change in the mode of fracture, Fig. 2. Fracture was initiated by nucleation of voids around undissolved carbide particles as shown in Fig. 2(a).

Fracture features of quasi-cleavage were observed for the 2200°F austenitizing treatment, Fig. 2(b).

An increase of room temperature K_{IC} with austenitizing temperature was also observed for steel B (See Table I below), as shown in Fig. 3. Also plotted in the figure are the K_{IC} values for steel D which showed little change with increase in austenitizing temperature. The reasons for the unexpected behavior of steel D are being sought.

Steels austenitized at 2200°F and ice brine quenched were tempered for one hour at both 400 and 575°F and the room temperature K_{IC} values determined, see Table II. In all cases the K_{IC} was higher in tempered specimens, relative to the as-quenched.

3. RELATIONSHIP BETWEEN FATIGUE CRACK GROWTH RATE AND MICROSTRUCTURE IN A SECONDARY HARDENING STEEL

Ronald M. Horn

The relationship between microstructure and fatigue crack growth rate is being studied in a 5Mo-0.3%C steel. Recently it was shown¹ that the fracture toughness of this steel varied with the austenitizing temperature. In the present study, the microstructures studied were those effected by austenitizing treatments at 1600 and 2200°F. The study also included five tempered conditions with each austenitizing treatment. These treatments produced a variety of microstructures. The high temperature austenitizing treatment produced a larger grain size and, possibly, a different carbon distribution which might influence the

Table II. The effect of tempering on the room temperature plane strain fracture toughness (ksi-in.^{1/2}) of steels austenitized at 2200°F and ice brine quenched.

Steel designation	As austenitized and quenched	Tempering temperature (°F)	
		400	575
A	100	109	107
B	70	101	93
C	113.5	128.3	118
D	55.2	96.9	---

Table I. Fatigue crack growth properties.

A. Fe-5Mo-0.3C Steel --Austenitized at 2200°F						
Specimen	Tempering Temperature, °C(°F)	Co	n	ΔK (ksi-in. ^{1/2}) for da/dN (in/cycle)		
				5×10^{-6}	1×10^{-5}	5×10^{-5}
5-3-1	as quenched	1.87×10^{-15}	2.2	22.40	31.30	64.40
8-5-2	225 (425)	1.31×10^{-14}	2.0	21.90	31.60	72.50
5-2-3	300 (572)	1.85×10^{-15}	2.1	24.00	33.90	70.80
8-2-4	500 (932)	1.06×10^{-15}	2.3	15.90	21.90	43.60

B. Fe-5Mo-0.3 Steel --Austenitized at 1600°F						
Specimen	Tempering Temperature, °C(°F)	Co	n	ΔK (ksi-in. ^{1/2}) for da/dN (in/cycle)		
				5×10^{-6}	1×10^{-5}	5×10^{-5}
18-6-2	as quenched	1.47×10^{-21}	3.5	32.40	39.80	63.10
18-6-3	225 (435)	9.16×10^{-20}	3.1	30.20	38.00	63.90
18-6-6	300 (572)	1.97×10^{-20}	3.2	30.90	38.90	63.90
15-6-8	500 (932)	2.09×10^{-20}	3.2	29.90	37.20	62.50
18-6-0	600 (1112)	3.50×10^{-20}	3.2	25.40	31.60	41.20

martensite structure and the subsequent tempering reactions.

Preliminary observations of fatigue crack propagation indicated distinct differences in crack growth rates for the two austenitizing treatments. Crack growth rates, da/dN were related to stress intensities, ΔK , by the equation

$$\frac{da}{dN} = Co (\Delta K)^n$$

The coefficients Co and exponents n were estimated. The data are summarized in Table I. The distinct difference in the exponents for the two austenitizing treatments was

attributed to a difference in the mechanism for crack growth. Changes in growth rates were also observed with changes in tempering temperature; high tempering temperatures had adverse effects.

Research in progress is aimed at obtaining more crack growth data in order to characterize microstructural features with mechanisms of crack propagation and fracture.

1. R. D. Goolsby, Relationships Between Microstructure and Fracture Toughness in a Secondary Hardening Steel (Ph.D. thesis), University of California, Berkeley, LBL-405, Nov. 1971.

4. THE INFLUENCE OF COOLING RATE IN A JOMINY TEST ON TOUGHNESS OF STEELS

Roy N. Lott

The objective of this study was to examine critically the Jominy end quench test as a design criterion. Jominy curves of steels are used to predict properties of quenched parts. The measured hardness at any point of interest on the part is transferred to the Jominy curve to obtain the cooling rate at 1300°F. From the hardness and the cooling rate at 1300°F., attempts are made to predict the properties of the quenched part. Jominy

Fig. 1. Sketch of the modified end quench specimen showing the location of the Charpy V-notch bars cut from it. (XBL 731-5655)

curves have been based on the cooling rate at 1300°F, because the cooling rate at this point determines whether or not the cooling curve passes through the pearlite knee in the TTT diagram of the steel. However, austenite to bainite and/or to martensite transformations occur below the pearlite knee and the cooling rate at lower temperatures should influence the final properties of the steel by its effect on the amount and type of bainite and martensite formed.

In the present investigation, the end quench specimen was modified to a rectangular bar so it could be cut into Charpy V-notch bars after the end quench heat treatment, Fig. 1. These involve cooling curve determinations for bar center and half-radius positions in bars of diameters 1 in., 2 in., 2 1/2 in., and 3 in. Cooling rate vs bar diameter and cooling rate at 1300°F vs cooling rate at a temperature in the bainite region can be determined from the above experiments. Following the same procedure for cooling curves obtained at points on the end quench specimen, a comparison of the curves should help indicate the fallacy of prediction of microstructure and properties from the cooling

Fig. 2. Cooling rate at 1300 and 700°F vs distance from quenched end in the modified Jominy bar of the present investigation. Also shown are the 1300°F data for a standard Jominy bar. (XBL 731-5656)

Table I. Charpy toughness data for AISI 4130 steel as a function of test temperature and position along the end quench bar (specimen numbers correspond to positions as indicated in Fig. 1).

Heat treatment	Specimen No.	Charpy V-notch energy (ft lb) at test temperature (°F).			
		RT	150	212	392
Standard quench	1	10.6	23.7	17.5	20.5
	2	16.9	55.1	71.5	93.2
	3	17.9		78.5	95.0
	4	17.7		67.0	77.0
	5	14.5	42.0	57.5	65.0
	6	17.3	42.0	55.5	59.0
	7	19.3	39.2	57.1	61.5
	8	20.0	36.5	61.4	64.0

	Specimen No.	RT	150	212	392
Step quench	1	10.0	15.0	12.0	14.0
	2	5.1	11.0	17.5	32.5
	3	6.6	17.0	21.0	50.0
	4	8.0	12.5	24.5	52.5
	5	8.0	11.2	31.5	55.5
	6	6.9	19.5	29.0	54.5
	7	7.7	13.2	30.0	54.5
	8	6.2	16.0	31.5	55.0

Fig. 3. Hardness vs distance from quenched end of the modified Jominy bar of AISI 4340 steel austenitized and quenched as indicated. The broken lines are the specified limits of hardness for a standard Jominy bar of this steel.
(XBL 731-5657)

Table II. Charpy toughness data for AISI 4340 steel as a function of test temperature and position along the end quench bar (specimen numbers correspond to positions as indicated in Fig. 1).

Heat treatment	Specimen No.	Charpy V-notch energy (ft lb) at test temperature (°F)			
		RT	150	212	392
Standard quench	1	4.2	5.2	5.0	16.0
	2	6.3	6.2	7.5	10.6
	3	6.2	5.7	7.0	9.4
	4	5.9	5.4	7.0	9.9
	5	5.4	6.2	6.4	12.5
	6	5.5	6.5	6.4	21.5
	7	5.6	6.4	8.0	21.0
	8	5.5	6.6	8.0	23.0

	Specimen No.	RT	150	212	392
Step quench	1	5.0	6.8	8.0	13.5
	2	6.9	7.8	9.5	11.5
	3	6.0	7.2	8.5	10.5
	4	5.5	12.7	7.5	9.0
	5	6.9	8.8	10.0	12.5
	6	6.6	10.3	13.0	21.0
	7	9.1	7.4	11.0	27.5
	8	5.8	7.4	11.0	30.0

Fig. 4. Hardness vs distance from quenched end of the modified Jominy bar of AISI 4130 steel austenitized and quenched as indicated. The broken lines are the specified limits of hardness for a standard Jominy bar of this steel. (XBL 731-5658)

rate at 1300°F. Specimens were quenched in an end quench rig modified for rectangular specimens with a slit instead of a round nozzle. The behavior of two steels, AISI 4130 and 4340, was examined in the present investigation.

It has been shown that the toughness of AISI 4130 and 4340 steels are greatly improved by austenizing at 2200°F and step quenching to the commonly used austenizing temperature (1600, 1550°F respectively) before quenching them to room temperature. Accordingly, one set of specimens of each alloy was step quenched (1 hr at 2200°F + 1/2 hr 1550 or 1600°F + end quench) and the other set was given the standard heat treatment (1/2 hr 1550 or 1600°F + end quench). The rectangular end quench specimens of both alloys conformed closely to the standard Jominy end quench as demonstrated by the cooling rate curves in Fig. 2 and the hardness curves in Figs. 3 and 4. Charpy V-notch bars cut from the end quenched specimens (see Fig. 1) were broken at temperatures selected so that the ductile-brittle transition curve could be determined for each position on the end quenched specimen for each alloy and heat treatment. Table I shows the Charpy-V-notch values of AISI 4130 steel in both the standard quenched and step quenched conditions. Table II shows the Charpy test data for AISI 4340 steel.

Experiments to determine the cooling curves of round bar sections quenched in agitated oil and agitated water are now in progress.

1. W. E. Wood, Ph.D. thesis, University of California, Berkeley (LBL-1474).

5. DESIGN OF INTERSTITIAL-FREE CRYOGENIC ALLOYS

Michael J. Yokota, Wade A. Horwood, and Go Sasaki

The mechanical behavior of metals at cryogenic temperatures is of technological importance as well as of scientific interest. With the rapidly expanding use of liquefied gases in scientific and industrial applications there is a great demand for materials which are both tough and strong at temperatures down to -200°C. Examples include container material for propellants used in space and missile systems and for use in the storage and transportation of liquid natural gases.

Presently available materials fall into

two classes: 1) those that show very high strength but low toughness and which generally have a body centered cubic matrix, and 2) those that show high toughness but relatively low strength and have a face centered cubic structure. Our initial approach has been to investigate bcc iron-based alloys with the purpose of developing exceptional combinations of high strength as well as high resistance to catastrophic brittle failure at low temperatures. This research approach reduces to the fundamental problem of decreasing the ductile-brittle transition temperature in basically body centered cubic structures. A number of factors are known to influence the low temperature toughness of bcc iron and its ductile-brittle transition temperature. Of these the role of

- 1) interstitial elements,
- 2) substitutional elements,
- 3) grain structure, and
- 4) dislocation substructure

were felt to be of primary importance. Based on the above considerations a Fe-12%Ni-0.5%Ti alloy was selected for study.

The addition of 12%Ni (factor 2 above)

Fig. 1. Portion of a tentative phase diagram of the Fe-Ni-Ti system showing the transformation temperatures for the Fe-12Ni-0.5Ti alloy. (XEL 731-5660)

serves several functions. A unique toughening is produced in nickel containing ferritic steels at low temperatures. Only manganese and, possibly, several elements of the platinum group have comparable effects on iron. Secondly, with the addition of 12%Ni, the equilibrium two phase $\alpha + \gamma$ field widens abruptly while also being lowered by several hundred degrees, Fig. 1. This feature of the alloy allows for possible grain refinement (factor 3 above) by a phase transformation-recrystallization process, which is part of the present investigation and is discussed in a later section.

Titanium was added to act as a scavenger for impurities, especially interstitials (factor 1 above) and also to achieve strengthening via solid solution and precipitation hardening. A low free-interstitial content was felt to be of primary importance in producing good notch toughness at low temperatures. Additional strengthening by Ti was also felt to be desirable to compensate for the removal of carbon in its usual role as a hardening element in steels.

The purpose of the above considerations was to produce a matrix structure which would exhibit good resistance to brittle fracture

at low temperatures. A further improvement in notch toughness could be attained by optimizing the microstructure features such as grain size and dislocation substructure (factors 3 and 4 above) through thermal and mechanical treatments.

The notch toughness of several commercial bcc iron-based alloys are modestly improved by a reheating treatment usually several hundred degrees below the equilibrium austenite phase field. A number of reasons have been given to explain this phenomenon but none seem to apply generally in all cases. Figure 2(a) shows the effect of reheating temperature on the energy absorbed at liquid N₂ temperature by standard Charpy V-notch specimens of the Fe-12%Ni-0.5%Ti alloy. Specimens were initially austenitized at 900°C for two hours and air cooled. The reheating temperature corresponding to the maximum Charpy V-notch energy was in the temperature range for rapid martensite to austenite transformation.

Optical examination of the 700 and 750°C reheated structures showed that grain refinement from an austenite grain size of 50 μ m to a reheated grain size of 10 μ m occurred during the $\alpha + \gamma$ transformation. The grain

Fig. 2. The effect of reheating temperature on (a) the Charpy V-notch energy at -196°C and the grain size, and (b) the room temperature hardness and the -196°C yield strength, of the Fe-12Ni-0.5Ti alloy.

(XBL 731-5659)

size is plotted against the reheating temperature in Fig. 2(a). For lower reheating temperatures in the equilibrium $\alpha + \gamma$ temperature range, some $\alpha \rightarrow \gamma$ transformation took place. However, no grain refinement was observed, Fig. 3. Another observation that can be made from Fig. 3 is the precipitation of Ni_3Ti in the α phase. These precipitates were not present in the 700 and 750°C reheated microstructures. Higher reheating temperatures above 750°C produced rapid grain growth. Figure 2(b) shows variation of hardness and yield strength with reheating temperature. Note that the 650°C reheating, which produced a structure with precipitate, gave a yield strength 10,000 psi greater than those for the 700 and 750°C reheating treatments which produced grain refinement with no precipitation. These initial results suggested that a two-stage heat treatment including grain refinement in the temperature range 700-750°C and precipitation hardening below 650°C would be beneficial in optimizing both strength and toughness. Figure 3 is an example of this type of microstructure. For specimens with this microstructure, yield strength of 150 ksi, and Charpy impact value of 150 ft-lb were attained at liquid N_2 temperature. It was believed that the usual deterioration of notch toughness from precipitation aging (grain boundary pre-precipitation) was avoided in the present case by the formation of non-precipitated (transformed austenite) regions along the grain boundaries, during the aging step.

The above results showed that a fivefold increase in grain refinement resulted through a single cycle into the $\alpha + \gamma$ phase region. Past studies on other systems suggest that repeated cycling can further refine grain size. Initial results on the present system confirmed this view. Hot working in the $\alpha + \gamma$ two-phase region or cold working followed by direct reheating to the precipitation aging temperature range also showed promising microstructures and are thus providing a number of processing methods to achieve the desired microstructure. Each of these techniques may be useful for a particular industrial application.

Future research activity will concentrate on maximizing yield strength and notch toughness in the manner described above for a given range of service temperatures. This will entail work on higher Ti concentrations in Fe-Ni alloys with both higher and lower concentrations of Ni than the 12% alloy described here. The principles used in developing the present Fe-Ni-Ti system will be expanded to include other promising alloy systems, e.g., the Fe-Mn-Ti system.

Fig. 3. Transmission electron micrographs of carbon replicas showing the microstructure of the Fe-12Ni-0.5Ti alloy.

(a) Austenitized at 900°C and reheated at 650°C for 2 hr. Charpy V-notch energy at -196°C was 10 ft lb.

(b) Austenitized at 900°C, reheated at 700°C for 2 hr and then at 650°C for 2 hr. Charpy V-notch energy at -196°C was 150 ft lb. (XBB 731-378)

6. MECHANICAL PROPERTIES OF THE CRYOGENIC ALLOY Fe-12Ni-0.25Ti

Sunguo Jin and John W. Morris*

The excellent combinations, strength and toughness of the Fe-12Ni-0.5Ti alloy at temperatures down to -196°C have been discussed in an earlier section. The optimum heat treatment for this alloy was a 2 hr austenitizing treatment followed by a 2 hr anneal at 750°C. With this heat treatment, the Charpy V-notch energy value at liquid helium temperature (6°K) was good (45-60 ft lb), though less spectacular than the value at -196°C (130-160 ft lb). The function of 0.5% Ti in the alloy was to act as a scavenger of impurities and also to impart solid solution and precipitation hardening (196 ksi yield strength at 7°K).

It was believed that decreasing the Ti content to 0.25% would considerably improve the toughness at 6°K without causing an

appreciable decrease in strength. The grain size was further reduced by a 30% cold work at room temperature before the final anneal. The final treatment of Fe-12 Ni-0.25 Ti alloy consisted of the following steps:

- (1) Forge at 1100°C and air cool.
- (2) Anneal at 700°C for 2 hr and ice brine quench.
- (3) Cold work 30% at room temperature.
- (4) Anneal at 700°C for 2 hr and ice brine quench.

The 6°K Charpy V-notch energy was 172 ft lb and the yield strength was 185 ksi for the specimen heat treated as above. The grain size was estimated to be 10 μ . A two hour post processing treatment in the 550-650°C temperature range caused the nucleation of extremely fine (0.5 μ) grains of the γ phase at the boundaries of the existing 10 μ grains of the α phase. On cooling from the 550-650°C range, the γ phase transformed to α , and the room temperature microstructure consisted of 10 μ grains of α decorated at the boundaries by 0.5 μ grains of α . Charpy energy values greater than 225 ft lb at 77°K and 220-225 ft lb at 6°K were attained when the post processing step was added to the heat treatment.

Research in progress is aimed at eliminating the mechanical processing and using thermal cycling to attain fine grain size. Preliminary grain size studies have indicated that alternate 700 and 600°C one hour annealing treatments with intermediate brine quenches decrease the grain size to the range 0.3-0.7 μ . The influence of this heat treatment on the microstructure and mechanical properties of the Fe-12Ni-0.25Ti alloy is under investigation.

* This work was the joint effort of principal investigators Parker, Zackay, and Morris.

7. STRUCTURE AND MECHANICAL PROPERTIES OF NON-CARBON-CONTAINING FERRITIC ALLOYS AT ROOM AND ELEVATED TEMPERATURES

Dilip Bhandarkar and Manjeshwar S. Bhat

Most commercial creep resistant materials derive their strength from a fine dispersion of a second phase which hinders the movement of dislocations. In creep resistant ferritic steels, the fine dispersion almost invariably consists of carbides. The morphology and composition of carbide particles tend to change slowly at elevated temperatures and

this often results in an increase in creep rate. The concept of using intermetallic compounds, rather than carbides, for increasing the high temperature strength of alloys is decades old, but progress has been slow. The class of compounds known as the Laves phase have been considered for enhancing elevated temperature properties. Other investigators have concluded that, in general, when the Laves phase is present in significant amounts it can degrade room temperature ductility with little effect on creep properties. The results from the present investigation show, however, that with microstructural control, satisfactory values of room temperature strength and ductility, as well as good stress-rupture life, can be attained in very low carbon Fe-Ta alloys strengthened with the Laves phase Fe₂Ta.

Recently it was demonstrated by Jones et al.¹ that in iron-rich alloys of the Fe-Ta system, the brittleness due to the presence of the continuous network of the Laves phase at the ferrite grain boundaries could be overcome by a simple $\alpha + \gamma + \alpha$ heat treatment which spheroidized the precipitate. The alloys were then found to possess good room temperature ductility and tensile strength. Short time tensile tests at elevated temperatures indicated a gradual decrease in strength up to 600°C, then a sharp decrease as the test temperature was raised to 700°C. The temperatures for the $\alpha + \gamma$ and $\gamma + \delta$ phase changes were high in binary iron-tantalum alloys, and it was considered desirable to lower these temperatures to a range more suitable for heat treatments by adding a third element to the alloy. Chromium was chosen for this purpose because it is known to enhance also the oxidation resistance which is essential for elevated temperature applications.

Investigations of structure and short time tensile properties were carried out on alloys of iron containing 1 at.% tantalum and chromium contents up to 7 at.%. The structure of the Fe-17Ta-7Cr alloy is shown in Fig. 1(a) after solution treating at 1320°C (in the δ phase field) for one hour and aging at 700°C (in the $\alpha + \text{Fe}_2\text{Ta}$ phase field) for 40 minutes, and in Fig. 1(b) after spheroidizing at 1100°C (in the $\gamma + \text{Fe}_2\text{Ta}$ phase field) for 10 minutes following the aging treatment. The spheroidizing heat treatment not only eliminated the continuous grain boundary layer of Fe₂Ta, but also resulted in grain refinement. Similar changes were observed in the other alloys that were investigated.

The short time yield strength is plotted

Fig. 1. Microstructures of the Fe-1Ta-7Cr alloy (a) aged at 700°C for 40 minutes and (b) aged at 700°C and spheroidized at 1100°C for 10 minutes. (XBB 7210-4984)

Fig. 2. Yield strength (0.2% offset) as a function of the test temperature for alloys Fe-1Ta, Fe-1Ta-5Cr, and Fe-1Ta-7Cr spheroidized at 1100°C for 10 minutes. (XBL 731-5601)

as a function of the test temperature in Fig. 2 for the alloys Fe-1Ta, Fe-1Ta-5Cr and Fe-1Ta-7Cr that were spheroidized before testing. The yield strength did not drop precipitously until a temperature of about 700°C was reached. The Fe-1Ta-7Cr alloy was considerably stronger than the Fe-1Ta alloy. Creep and stress rupture tests were carried out on the Fe-1Ta-7Cr alloy at 538°C (1000°F) and 593°C (1100°F). Stress vs time to rupture data are plotted in Figs. 3 and 4. Also shown are the stress-rupture properties reported in the literature for 1Cr-1Mo-0.25V steel and 403, 410, and 422 type stainless steels. Both at 1000 and 1100°F, the Fe-1Ta-7Cr alloy results were above those reported for the 403 and 410 stainless steels, but below those for the 422 stainless steel and the 1Cr-1Mo-0.25V steel. Also shown in Fig. 4 are the preliminary stress-rupture data on a Fe-1Ta-7Cr-0.5Mo alloy which was developed along the same lines as the Fe-1Ta-7Cr alloy.

Fig. 3. Stress vs rupture time at 1000°F (538°C) for the spheroidized Fe-1Ta-7Cr alloy. Also shown are the results reported in the literature for the 1Cr-1Mo-0.25V steel and the 403, 410, and 422 type stainless steels. (XBL 7210-7053)

Fig. 4. Stress vs rupture time at 1100°F (593°C) for the alloys mentioned in Fig. 3. Also shown are the preliminary results on the Fe-1Ta-7Cr-0.5Mo alloy. (XBL 7210-7054)

The addition of molybdenum was made to obtain additional solid solution strengthening of the ferrite. Considerable improvements in stress-rupture properties were achieved as can be seen from Fig. 4.

Research is now in progress to optimize the heat treating procedure for the alloys Fe-1Ta-7Cr and Fe-1Ta-7Cr-0.5Mo. It was observed that by repeated cycling through the $\alpha + \gamma + \alpha$ phase transformation an extremely fine grain size was attained with a structure similar to a massive martensitic structure. It is of interest to investigate

whether such a structure is beneficial for creep properties. Another area of interest is to examine the possibility of using the Fe_2Ta dispersion to pin down the irregular grain boundaries resulting from the $\alpha + \gamma + \alpha$ transformation. Preliminary studies indicate that such a possibility exists, but certain modifications are needed in the heat treating temperatures and times.

1. R. H. Jones, E. R. Parker, and V. F. Zackay, Use of an Allotropic Phase Change to Enhance Ductility in Fe-Ta Alloys, Proc. Fifth Intern. Materials Symp., Berkeley, Calif., September 1971, p. 829.

8. STRUCTURE AND MECHANICAL PROPERTIES OF TRIP STEELS PROCESSED BY DEFORMATION AND THERMAL CYCLING

Howard E. Adkins, Jr. and Dilip Bhandarkar

Metastable austenitic steels with excellent combinations of strength and fracture toughness owe their unique properties to the deformation-induced transformation of austenite to martensite. Earlier investigations of these steels, known as TRIP steels, have shown that the mechanical properties are strongly dependent on such variables as the chemical composition and the thermomechanical processing. An important step in the processing is the prior deformation of austenite. This consists of deforming the austenitic steel up to an 80% reduction in thickness by rolling above the M_d , which is the temperature above which no martensite can be produced by deformation of the austenite. The primary purpose of the prior deformation is to increase the yield strength of austenite.

Recently, Koppenaal¹ showed that an increase in the strength of austenite could be obtained by thermally cycling the alloy between a temperature within the $M_s - M_f$ range and the temperature at which martensite reverts to austenite by reverse shear. The reversion results in a change in crystal structure from the body centered tetragonal to the face centered cubic while maintaining the high dislocation density associated with the martensite structure. Koppenaal concluded that the process could be conveniently applied only to steels which had their M_s temperature above -196°C .

The present investigation deals with the development of an alternate approach to apply the process of reversion to TRIP steels, some of which have their M_s below -196°C .

The approach is based on the fact that the deformation-induced transformation of austenite to martensite is strongly dependent on the stability of the alloy. It was shown by Bhandarkar et al.² that in TRIP steels of low stability, a large amount of martensite formed on the application of a very low stress at temperatures above the M_s , but well below the M_d .

Two TRIP steels were designed to have a low stability by adjusting the chemical compositions which are given in Table I. The first step in the processing was to deform the annealed steels (austenitic) by rolling 5-10% at cryogenic temperatures (-196 and -78°C) to form large amounts of martensite. The purpose of the above step was to attain a high dislocation density in the alloy from both the martensite formation and the deformation. The steels were then heated to temperatures between 750 and 800°C and held for short intervals of time to revert the martensite to austenite. Though complete reversion of martensite was desired, it was not achieved in the present investigation. Subsequent repetitions of the process of deformation and thermal cycling were carried out on each alloy and the room temperature tensile properties were determined after each complete cycle. Several variations of the normal cycling procedure were investigated in an attempt to optimize the mechanical properties. Yield strengths up to $140,000$ psi and ultimate tensile strength up to $220,000$ psi were attained. One of the problems associated with thermal cycling was the carbide precipitation which caused the depletion of the austenite stabilizing elements from the matrix. On testing at room temperature, the unstable austenite in the steel transformed to martensite at very low stresses and the transformation caused gross yielding of the tensile specimen. Several specimens tested at 100°C exhibited a higher yield strength than that at room temperature. At 100°C the austenite was more stable than at room temperature and a higher stress was required to initiate its transformation to martensite.

Table I. Chemical compositions of steels.

Alloy designation	Compositions (wt%)				
	C	Cr	Ni	Mn	Mo
A	0.28	12.0	7.8	1.9	---
B	0.30	9.0	7.8	2.0	2.0

1. T. J. Koppenaal, A Thermal Processing Technique for TRIP Steels, *Met. Trans.* **3**, 1549 (1972).

2. D. Bhandarkar, V. F. Zackay, and E. R. Parker, Stability and Mechanical Properties of Some Metastable Austenitic Steels, *Met. Trans.* **3**, 2619 (1972).

9. DESIGN OF HIGH MANGANESE METASTABLE AUSTENITIC STEELS

David G. Atteridge

A major stumbling block to increased industrial use of TRIP steels is the high cost of alloying elements and the processing. A typical TRIP steel contains 9% Cr, 8% Ni, 3% Mo, 2% Mn, and 0.3% C. Nickel and molybdenum are particularly expensive. Typical processing requires an 80% reduction in thickness by warm rolling at 450°C and involves high-strength rolls and high load capacity mills. The present investigation deals with the application of alloy theory and use of the TRIP phenomenon to develop steels with substantially reduced cost from the standpoint of both alloying and processing.

A series of Fe-12% Mn alloys with carbon contents from zero to 1.3% were selected for the present investigation. The equilibrium phase diagram of the Fe-12% Mn-x% C system predicts structures that are multiphase containing ferrite, austenite, and carbide in varying proportions, depending on the carbon content, as shown in Fig. 1. The austenite in certain alloys of this system is metastable and undergoes a strain-induced transformation to body centered tetragonal martensite. Following an austenitizing treatment, the alloys were deformed by rolling at several different temperatures. The role of the deformation on structure of alloys was twofold. First, deformation of an alloy in a phase field where part of the structure was austenitic resulted in a partial transformation of the austenite to body centered tetragonal martensite. Secondly, chemical changes, in the form of carbide precipitation, occurred in carbon-containing alloys and these in turn caused a decrease in stability of the alloy as a result of depletion of alloying elements.

The carbonless Fe-12% Mn alloy showed a continuous decrease in yield strength and ultimate strengths and an increase in the percent elongation as the rolling temperature was

Fig. 1. Vertical section of the ternary diagram of the Fe-12% Mn-x% C system. (XBL 731-5646)

raised. The rate of formation of martensite with strain during testing increased with an increase in rolling temperature, while the volume fraction of martensite at fracture decreased.

The 0.2% C alloy was magnetic at room temperature when slowly cooled from the austenitic region. Deformation by rolling in the austenitic region, however, mechanically stabilized the alloy and the deformed alloy remained austenitic at room temperature. The austenite was unstable and on testing at room temperature it exhibited a stress-induced martensitic transformation. This resulted in a low yield strength and a high ultimate strength.

A comparison of the yield strengths of alloys with different carbon contents, rolled at the same temperature, showed an increase in yield strength as the carbon content increased. The percent elongation was the largest for metastable austenitic alloys that were produced by rolling in the austenite phase field and smallest for alloys rolled in the three-phase austenite-ferrite-carbide region.

Based on the mechanical properties and the transformation behavior that were observed, a two-stage rolling schedule was designed. The alloy was first rolled 62% at either 950 or 750°C and then at temperatures ranging from 150 to 550°C until a cumulative reduction of 80% was attained. For the 0.2% C alloy rolled in two stages at 750 and 400°C, a yield strength of 165,000 psi, an ultimate strength of 230,000 psi, and an elongation of 17% were observed. The higher rolling temperature (at 750°C) results, of course, in lower roll separation forces and is therefore a desirable processing feature. The results were encouraging and further research is in progress.

10. ISOTHERMAL STUDIES OF PHASE TRANSFORMATIONS IN STEELS

B. Naga Prakash Babu

The conventional methods of plotting an I-T diagram are characterized by poor accuracy, are extremely slow and tedious, and require the metallographic examination of a series of samples reacted for various times. Also, it is possible that the interruption, by quenching, of the reaction for examination of structure would change the kinetics. An alternative approach is to observe the change of some property associated with a phase change in the sample. The method presented here consists of continuously recording the change in the magnetic susceptibility of the sample undergoing austenite transformation. For a given alloy, the magnetic susceptibility is a function of temperature, strain, and structure of the phases present.

The apparatus consisted of an inductor coil, 5 in. long and 2 in. in internal diameter, oscillating at 1.4 kHz, and generating a weak field around the sample. The coil surrounded a 1 in. outside diameter stainless steel tube, into which a sample strip of dimensions 3 in. $\times$ 1/2 in. $\times$ 0.03 in. was quenched. To maintain isothermal conditions, and to obtain a rapid quench, the quenching medium was circulated through the tube by pumping it from a heated reservoir. The sample was austenitized and dropped into the coil zone of the tube. The change in the magnetic susceptibility of the sample caused a change in the inductance of the coil, which, in turn, changed the frequency of a reference oscillator. The period of oscillation was measured by a time interval counter, a crystal oscillator providing a constant time base. The digital output from the counter was fed into a tape punch. The

Fig. 1. (a) Percentage of austenite isothermally transformed as estimated from the magnetic susceptibility change.

(b) The I-T diagram of AISI 4340 steel plotted from the data in Fig. 1(a).
(XBL 761-5644)

punch recorded the austenite decomposition continuously at intervals of 0.77 sec, 7.7 sec, or 77 sec. To interpret the data quantitatively, a calibration was needed for the temperature dependence of the magnetic susceptibility. For this reason the data obtained at different temperatures were normalized to a single temperature.

Research is in progress to use the technique to study the bainite and martensite transformations in a commercial AISI 4340 steel. The results presented here are tentative, because the curves of percent austenite transformed as estimated from the isothermal susceptibility data obtained at different temperatures were only approximately

normalized to room temperature. Figure 1(a) shows the various isothermal curves and Fig. 1(b) gives the I-T diagram derived from Fig. 1(a).

The martensitic reaction in this low alloy steel was believed to be athermal. The bainite nose of the I-T diagram for AISI 4340 shown in Fig. 1(b) is very much the same as the one in I-T diagrams determined by other investigators. Between 250 and 300°C, it is believed that there was a martensitic reaction in the first 15 seconds, and then the reaction proceeded by a bainitic mode. Also, the bainitic reaction was complete within an hour between temperatures 300 and 400°C. Above 400°C the bainitic transformation was incomplete. At 490°C there appeared to be an onset of the pearlitic mode of transformation, after partial bainitic transformation.

11. RESEARCH PLANS FOR CALENDAR YEAR 1973

Victor F. Zackay and Earl R. Parker

Further studies of the influence of microstructure and composition on the fracture toughness and fatigue crack propagation of ultra-high strength steels are planned for the coming year. In particular, the effect of impurities and inclusions on the fracture toughness of AISI 4130 and AISI 4340 will be investigated. Studies of the tempering behavior of secondary hardening steels will be continued. Additional studies of the phase transformations in cryogenic iron-nickel-titanium alloys will be made in order to get microstructures that are beneficial for high toughness and strength at temperatures down to that of liquid helium. A new project will be initiated with an objective of designing iron-manganese-titanium alloys for cryogenic applications. The research on elevated temperature alloys will involve further optimization of composition and microstructure in order to improve the stress rupture properties of Fe-Ta-Cr-Mo alloys.

12. 1972 PUBLICATIONS AND REPORTS

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

Journals and books

1. R. D. Goolsby, W. E. Wood, E. R. Parker, and V. F. Zackay, "Effect of Lath Boundary Precipitation on Fracture Toughness of Martensite," The Structure and Properties of

Materials--Techniques and Applications of Electron Microscopy, University of California, Berkeley, September 13-17, 1971, edited by G. Thomas (University of California Press, Berkeley, 1972), p. 798.

2. R. H. Jones, E. R. Parker, and V. F. Zackay, "Use of an Allotropic Phase Change to Enhance Ductility in Fe-Ta Alloys," ibid., p. 829.

3. W. W. Gerberich and V. F. Zackay, The Potential of Metastable High-Strength Fibers for Strong, Tough Composites, Met. Trans. 3, 747 (1972).

4. V. F. Zackay, E. R. Parker, R. D. Goolsby, and W. E. Wood, Untempered Ultra High Strength Steels of High Fracture Toughness, Nature Physical Science 236, 108 (1972).

5. D. Bhandarkar, V. F. Zackay, and E. R. Parker, Stability and Mechanical Properties of Some Metastable Austenitic Steels, Met. Trans. 3, 2619 (1972).

6. R. H. Jones, V. F. Zackay, and E. R. Parker, Laves Phase Precipitation in Fe-Ta Alloys, Met. Trans. 3, 2835 (1972).

Papers presented

1. E. R. Parker and V. F. Zackay, "Enhancement of Fracture Toughness in High Strength Steel by Microstructural Control," Symposium on Fracture and Fatigue, George Washington University, Washington, D. C., May 3-5, 1972. (LBL-832)

2. V. F. Zackay, E. R. Parker, and D. Bhandarkar, "The Structure and Properties of a Non-Carbon Containing BCC Iron Alloy at Room and Elevated Temperatures," Proc. The John E. Dorn Memorial Symposium on Rate Processes in Plastic Deformation, Cleveland, Ohio, October 16, 1972. (LBL-1178)

LBL reports

1. C. J. Bruggeman, The Effect of One-Dimensional Plane Strain Waves in α -Phase Titanium-Aluminum (Ph. D. thesis), LBL-802, April 1972.
2. A. J. Baghdasarian, Corrosion Resistance of TRIP Steels (M. S. thesis), LBL-806, June 1972.
3. M. W. Perra, Nuclear Magnetic Resonance Study of GP Zone Formation in Aluminum -4% Copper (M. S. thesis), LBL-838, June 1972.

4. R. A. McCoy and W. W. Gerberich,
Hydrogen Embrittlement Studies of a TRIP
Steel, LBL-439, July 1972 (accepted by
Met. Trans.).

5. W. A. Horwood, Factors Controlling the
Fracture Toughness of Cryogenic Alloys
(M. S. thesis), LBL-1121, Dec. 1972.

F. HIGH FIELD SUPERCONDUCTIVITY

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

1. INTRODUCTION

A composite superconducting tape,¹ consisting of thin filaments of Nb₃Sn dispersed in a niobium matrix, has been developed at IMRD. Much of the current work was directed towards improving the electrical properties of the tape. During the past year a sixfold increase in current-carrying capacity was achieved. Several means were found for increasing the volume fraction of Nb₃Sn in the composite. Present work on enhancing the critical current density of the Nb₃Sn filaments should lead to further improvement. Niobium powder is available from commercial suppliers in a rather limited range of particle size distributions. In an investigation of the possibility of using niobium hydride in place of elemental niobium powder, it was demonstrated that this substitution is entirely practicable. Furthermore, it was found that from the hydride any desired particle size range could be prepared here in the laboratory, as illustrated in Fig. 1. This of course provides much greater flexibility in optimizing the process variables.

1. M. R. Pickus, V. F. Zackay, E. R. Parker and J. T. Holthuis, A Powder Rolled Superconducting Composite with Controlled Morphology, LBL-821 preprint, August 1972. (scheduled for publication in the International Journal of Powder Metallurgy, January 1973.)

Fig. 1. Scanning electron micrographs of niobium hydride powder. (x 1000)
(a) As received from the supplier.
(b) Ball-milled 48 hours and treated with hot hydrochloric acid.

(XBB 731-371 & XBB 731-370)

2. EVALUATION OF OPTIMAL PARAMETERS FOR POWDER-ROLLED TAPE

Kanithi Hemachalam

A few illustrative results of this investigation are presented here. The ductility of the porous sintered niobium tape is an important consideration for two reasons:

- 1) The infiltrated tape must withstand a cold reduction in thickness of the order of 80% in order to impart to the infiltrated tin a filamentary morphology, and
- 2) The diffusion reacted tape must withstand the winding required to form solenoids. Samples of green tape were sintered for various times at several temperatures. Because of the physical dimensions of the tape, a standard tensile test for determining the percentage elongation was considered unsuitable. Instead, a somewhat crude but effective method was employed. A sintered specimen was bent around rods of varying diameter, beginning with the largest diameter. The diameter around which the bending resulted in a visible crack was designated as "The Critical Diameter." The relationship between critical diameter and sintering conditions is shown in Fig. 1.

As pointed out by Prakash Babu (LBL-437), there is a progressive reduction in the volume fraction of tin with increasing amounts

Fig. 1. Critical diameter (an indication of ductility) as a function of time at various temperatures.
 (XBL 7210-7044)

Fig. 2. Influence on volume fraction of Nb_3Sn of various methods of constraining tin loss due to plastic flow. (x500)

Filaments: Nb_3Sn ; Matrix: Niobium;
White: Unreacted tin.

(a) Normal processing: rolling at room temperature.

(b) Using a dilute (1-2%) solution of copper in tin as the infiltrant.

(c) Rolling the infiltrated tape at $-78^\circ C$.

(d) Cladding the infiltrated tape with niobium before rolling.

(XBB #'s 731-369, 368, 367, 366 respectively)

Fig. 3. Comparison of current-carrying capacity (dc) as a function of applied magnetic field for IMRD and General Electric Co. type 22CY0325 superconducting tapes. (XBL 731-5626)

of mechanical deformation. He found that tin from the pores had squeezed out to the surface during cold reduction, due to the difference in flow stresses of niobium and tin. Such losses, of course, have an adverse effect on the current-carrying capacity of the fully processed tape.

Several procedures for preventing this loss of tin were devised and investigated. A marked improvement was observed with the following methods:

- 1) Cladding the infiltrated tape with niobium or copper before rolling.
- 2) Performing the rolling cryogenically.
- 3) Hardening the infiltrated tin by alloying with copper.

Examples of the increase that has been achieved in the volume fraction of Nb_3Sn in the fully processed tape are shown in Fig. 2, for a reduction in thickness of 80%.

Figure 2(a) shows the tape after normal processing--rolling at room temperature with no special treatment. The sample shown in Fig. 2(b) was prepared by using a dilute solution of copper in tin for the infiltrant. The copper content was between 1 and 2% by

weight. For Fig. 2(c) the infiltrant was pure tin, but the reduction in thickness was carried out at -78°C . Cladding the infiltrated tape with niobium before the rolling was performed resulted in the structure shown in Fig. 2(d).

Other topics investigated and described in LBL-1108 include: the strength of the tape at sintering temperatures, a comparison of powder flow during rolling in air and vacuum, the influence of 60 cycle vibration on powder flow, along with a number of design considerations relevant to the preparation of continuous tape.

On the basis of the limited data presently available, a comparison of the critical current-applied magnetic field relationship for the newly developed, undoped, IMRD tape and General Electric Co.'s doped tape, one of the best of the commercially available tapes, is shown in Fig. 3. At low fields the influence of doping in increasing the critical current density of Nb_3Sn appears to be the dominant factor. As the strength of the magnetic field is increased the unique filamentary structure of the IMRD tape, even though undoped, rapidly exhibits its advantage as a high field superconductor, the crossover occurring at about 55 kG. It is anticipated that the advantage would be even more pronounced under ac conditions. Doping the IMRD tape, it is hoped, will retain the slope of the curve, but shift it upward to higher current values.

3. A NEW PROCESS FOR MAKING STABILIZED SUPERCONDUCTING TAPE

William H. Harris

The powder metallurgy method for making IMRD superconducting tape was modified to produce Nb_3Sn filaments interfaced with copper. It is believed that such a microstructure could desensitize Nb_3Sn with respect to instabilities such as short-term flux jumping. During such instabilities the copper interface would provide a low resistivity path for supercritical currents. This would have the effect of increasing the critical current density of the Nb_3Sn filaments.

For this purpose, the infiltrant employed was an alloy of 75 at.% tin and 25 at.% copper. The idea was that the tin would diffusion-react with the niobium, leaving the copper behind as an interface. With this alloy maintained at a temperature of 655°C , infiltration of the porous niobium was complete. Whereas Hemachalam, as

Fig. 1. Microstructure of IMRD superconducting tape showing Nb_3Sn filaments interfaced with copper. (x1000) (XBB 731-11)

previously noted, used small additions of copper for alloy hardening of the infiltrated tin in order to minimize its loss during rolling, the use of 25 at.% copper so hardened the tin that it became necessary to perform the rolling at elevated temperatures in order to obtain a filamentary microstructure. The rolling temperature of 480°C was selected on the basis of such considerations as the formation of undesired intermediate phases, optimum tin retention, and development of the desired microstructure. A diffusion-reacted composite consisting of a niobium matrix containing copper-interfaced filaments of Nb_3Sn is shown in Fig. 1.

Pulsed magnet tests to determine the critical current-critical field relationship are presently under way for samples with a 75, 85, and 95% reduction in thickness. Magnetic fields up to 200 kG will be employed.

4. THE NIOBIUM-MOLYBDENUM NITRIDE SYSTEM

Michael M. Collver, William H. Gourdin, Charles W. Krause and Steve Wilson

Some recently developed theoretical ideas indicate that the critical temperature, T_c , of niobium nitride should be increased by substituting molybdenum for some of the

niobium. A study of the ternary up to 15% molybdenum was therefore undertaken. The compounds were prepared by flowing nitrogen gas taken from above the liquid in a liquid nitrogen dewar over foils of the alloys under the following conditions: 10 minutes and 30 minutes at 1400°C and 30 minutes at 1550°C. The data indicate, rather than an increase, a progressive decrease in T_c , amounting to approximately 1.5°K for 15% molybdenum.

5. RESEARCH PLANS FOR CALENDAR YEAR 1973

Earl R. Parker, Victor F. Zackay, and Milton R. Pickus

Research will continue on optimization of IMRD superconducting tape. It has been reported that doping with certain elements, particularly zirconium, increases the current-carrying capacity of niobium-tin superconductors by a factor of 3-4. An investigation will be made to determine whether a comparable enhancement can be obtained for powder-rolled tapes. Two approaches will be used: zirconium will be added to the infiltrant tin bath, in one instance, and, in the other, a pre-alloyed niobium-zirconium powder will be used instead of the elemental niobium powder which is presently employed. The influence of zirconium on infiltration and diffusion kinetics will be determined for both approaches, in addition to its effect on current-carrying capacity.

Feasibility experiments are contemplated utilizing different compaction modes with the objective of designing a superconducting material better suited for ac applications. The present tape is a composite consisting of Nb₃Sn filaments dispersed in a niobium matrix. The filamentary structure is desirable. Unavoidably, however, the present

process leads to some cross-linking of the filaments--which is presumed to be undesirable for ac superconductors. The specific objective would be to develop a filamentary composite with no cross-linking.

The increase in current-carrying capacity already achieved has made necessary a modification of the current-source system of the pulsed magnet apparatus. The changes to make more amperes available will be effected as soon as possible, so that evaluation of both the niobium-tin-copper and the zirconium-doped tapes can be carried out.

As progress is made in the development of ac superconductors, provisions will have to be made for the performance of ac tests. Since data on the composites will be available from dc and pulsed magnet tests as well, an attempt should be made to establish the extent and validity of correlations between the various types of data, particularly with pulsed data as a reference.

6. 1972 PUBLICATIONS AND REPORTS

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

LBL reports

1. M. R. Pickus, V. F. Zackay, E. R. Parker, and J. T. Holthuis, A Powder Rolled Superconducting Composite with Controlled Morphology, LBL-821 August 1972 (submitted to Int'l Journal of Powder Metallurgy).

2. K. Hemachalam, Evaluation of Optimal Parameters for the Production of Superconducting Niobium-Tin Tape in Relation to Pilot Plant Design (M.S. thesis), LBL-1108, June 1972.

G. POWDER METALLURGY

Milton R. Pickus, Principal Investigator

1. INTRODUCTION

Milton R. Pickus

IMRD research in powder metallurgy (P/M), which in the past was limited to superconducting materials, is being broadened to encompass engineering alloy systems of a more generalized nature. Although P/M has become an important technology--from it have come, in addition to its intrinsic economies, such significant developments as the tungsten filaments for the incandescent lamp, the sintered carbides for cutting tools and wear-resistant dies, the self-lubricating bearing, the friction brakes for modern aircraft, to name but a few--its further development depends upon a systematic application of the principles of materials science. As compared with wrought materials, structural P/M products made by pressing and sintering are deficient in important mechanical properties such as ductility, fatigue strength and fracture toughness. To improve these properties current practice is to resort to secondary treatments which are costly and not always completely effective. There is a good possibility that this situation is simply a consequence of applying P/M techniques to the standard engineering alloys made by conventional processes with little, if any, modification. The objective of this aspect of research in P/M is to design alloy systems that are especially adapted to the sequence of powder compaction and sintering.

2. RESEARCH PLANS FOR CALENDAR YEAR 1973

Milton R. Pickus

a. Superconducting Materials by Powder Metallurgy

Research will continue on optimization of the powder-rolled superconducting tape developed at IMRD. Whereas the progress and research plans for superconducting materials are described in another part of this report under the title, "High Field Superconductivity," it may be briefly noted here that a sixfold increase in current-carrying capacity of the tape has been achieved during the past year. In the coming year feasibility experiments are contemplated to develop a superconducting material especially suited for ac applications.

b. Alloy Design for Powder Metallurgy

The initial effort will center on ferrous systems, because of their technological importance. It is generally considered, with much supporting evidence, that the deficiency in mechanical properties noted in the introduction is attributable to residual porosity. Most commercially produced P/M parts have an unintentional residual porosity of the order of 10% or more. In this range there is a substantial reduction in mechanical property values.

Two basic approaches to the problem of residual porosity have been critically examined:

1. Design alloy systems that are conducive to the attainment of near theoretical density.
2. Design alloy systems that have a marked insensitivity to the presence of residual pores.

A study of the available data as reported in the literature indicates that enhancement of fracture toughness should be regarded as an expedient rather than a basic solution. In those instances where fracture toughness, at a given level of residual porosity, has been increased by alloying, it has been found that the fracture toughness of the alloy rapidly increases still further as the porosity is decreased. Moreover, such fundamental material properties as Poisson's ratio and the modulus of elasticity, while insensitive to changes in composition or thermal treatment, are directly proportional to density. Tensile strength, yield strength, hardness, and elongation are all nearly proportional to density. Finally, impact strength appears to fall off exponentially with decreasing density.

It has been concluded, therefore, that the significant solution for the problem of residual porosity would be its elimination, and that investigating the means for achieving full density would be the focal point of this research effort.

To implement this objective, several methodologies will be employed. These include liquid phase sintering, dispersions of selected phases, doping, and the use of very fine powders.

As progress is made with simple alloy systems the results will be applied to more complex multi-element systems with emphasis on high strength and corrosion-resistant alloys.

H. THERMODYNAMICS OF METAL SYSTEMS

Ralph R. Hultgren, Principal Investigator

1. EVALUATION OF THERMODYNAMIC DATA

Ralph R. Hultgren and Pramod D. Desai

The evaluation of thermodynamic data for metallic systems was completed. The results are to be published in two volumes by the American Society for Metals, as follows:

I. Selected Values of the Thermodynamic Properties of the Elements (636 pp.), by Ralph R. Hultgren, Pramod D. Desai, Donald T. Hawkins, Molly Gleiser, Kenneth K. Kelley, and Donald D. Wagman.

Nonmetallic elements in this volume were evaluated by Donald D. Wagman of the National Bureau of Standards. This volume is now in press.

II. Selected Values of the Thermodynamic Properties of Binary Alloys (1435 pp.), by Ralph R. Hultgren, Pramod D. Desai, Donald T. Hawkins, Molly Gleiser, and Kenneth K. Kelley.

This volume is now in press.

2. METALS HANDBOOK PHASE DIAGRAMS

Donald T. Hawkins and Ralph R. Hultgren

Approximately 400 phase diagrams were edited and corrected for the forthcoming edition of Metals Handbook by the American Society for Metals. Of these, approximately 300 were taken from Selected Values of Thermodynamic Properties of Binary Alloys.

3. THERMODYNAMIC EVALUATION AND COMPILATION OF METAL ALLOY SYSTEMS

Leo Brewer and Ralph R. Hultgren

The bibliography of the literature pertaining to phase diagrams and thermodynamic data for metal alloy systems will be kept up to date, and evaluations of selected binary and ternary systems will be published periodically.

4. 1972 PUBLICATIONS AND REPORTS

Ralph R. Hultgren and Associates

In addition to the books mentioned previously, the following publications were produced.

Journals

1. H. I. Yoon and R. R. Hultgren, The Effect of Ordering on Lattice Heat Capacities of Ordered and Disordered AuCu₃, *J. Chem. Thermodynamics* 4, 375-380 (1972).

2. H. I. Yoon and R. R. Hultgren, Heats of Formation of Solid Indium-Lead Alloys, *J. Chem. Eng. Data* 17, 176-177 (1972).

3. J. Chipman, Thermodynamics and Phase Diagram of the Iron-Carbon System, *Met. Trans.* 3, 55 (1972).

LBL Reports

1. J. C. Cases, The Heat Content of NaNO₂ between 450 and 800 K, LBL-842, May 1972.

2. J. C. Cases, Diphenyl Ether, A Versatile Substance for Laboratory Demonstrations, LBL-868, June 1972.

I. ADVANCED MATERIALS

Robert H. Bragg, Principal Investigator

1. STRUCTURE AND PROPERTIES OF SOME ADVANCED MATERIALS

Robert H. Bragg

We have been studying the structure and properties of Glassy Carbon, GC, and Pyrolytic Graphite, PG, the former having properties totally different from conventional carbons and graphites, and the latter being similar to pure graphites. During the past year we have done a great deal of work, especially on pyrolytic graphite, and the combination of careful experiments and good theoretical work have produced a greatly enhanced and simplified technique of structural characterization. We have also continued our studies of unidirectional solidification of eutectics in order to produce unique microstructures with heretofore unobtainable properties. To date our experiments have been confined to the Al-CuAl₂ pseudo-binary eutectic, and significant progress has been made in identifying the factors governing eutectic solidification at high growth rates.

Excessive delays in the delivery of our low temperature electrical measurement apparatus have occurred, but compensating developments have rendered these delays irritating but not crippling. Significant comments are given in short reports given below.

2. STRUCTURE OF GLASSY CARBON

Madan M. Biswal and Robert H. Bragg

Work to date has shown that heat treatment of glassy carbon previously carbonized at 1000°C for one hour produces no perceptible changes in structure over long periods of time at temperatures below 2500°C. Heat treatments at 2700°C have been made but no analyses have been completed. No new evidence has been found which contradicts the inter wound spaghetti model for the pores in Glassy Carbon, but the heat treatments must be extended to at least 3000°C to complete the investigation.

3. SMALL-ANGLE SCATTERING BY ORIENTED ELLIPSOIDS

Faysal Hamzeh, Madan M. Biswal, and Robert H. Bragg

Small-angle scattering experiments reported in UCRL-20517 confirmed certain aspects of earlier results obtained on pyrolytic graphite by Bragg and co-workers. More careful experiments, over a larger angular range for which the intensity varies by a factor of 10⁴, confirmed the volume effect reported previously and revealed the expected deviation from the h^{-3} dependence of the intensity at large h [$h = (4\pi/\lambda)\sin \theta$], predicted by Porod, but left unexplained the significance of S in the Porod formula for oriented particles, even after corrections for local density fluctuations are made. New theoretical work reported in LBL-1176 and further work in progress provides a simple interpretation of both the Guinier and Porod regions of the scattering curve, and enables an unambiguous determination of the size and shape of the particles (voids in the case of PG) for ellipsoids of revolution of arbitrary shape. Additional new work now being written for publication extends the theory to general ellipsoids of semi-major axes a, b, c , all different, and the results reduce, for appropriate special cases, to those obtained for ellipsoids of revolution. Moreover, these results give a simple proof of Bragg's rule for small-angle scattering which had previously been established empirically.

4. UNIDIRECTIONAL SOLIDIFICATION OF Al-CuAl₂ EUTECTIC

Kwame Ankra and Robert H. Bragg

In this work, LBL-1182, banded microstructures were studied in the Al-CuAl₂ eutectic, unidirectionally solidified at large velocities (ca 200 cm/hr) in a horizontal direction in an open mold. Some new types of banding (see Fig. 1) were observed including a laminar-to-dendrite breakdown. (see Fig. 2) Some of the observations could not be explained by current theories or possible experimental errors. Analysis of the microstructures has eliminated all of

Fig. 1. Typical banded structure visible to the unaided eye. Mag. 45 $\times$ Growth direction is from bottom to top. (XBB 7210-5211)

Fig. 2. Longitudinal micrograph showing a eutectic-dendritic breakdown at a band. Growth direction is from bottom to top. Mag. 1420 $\times$ (XBC 726-3484)

the known theories, and a mechanism, based on convectional currents in the melt, is proposed but awaits experimental verification. This work was the M.S. thesis of Kwame Ankra, and is being written up, slightly revised, for publication.

5. OTHER WORK IN PROGRESS

Robert H. Bragg

Louis Salmon has completed his preliminary determination of the experimental conditions necessary to obtain well-aligned Al-CuAl₂ composites with arbitrarily chosen interlamellar spacings. Ram Saxena is investigating a recently observed acousto-electric effect in pyrolytic graphite in which pressure applied in the c-direction causes appreciable changes in the electrical conductivity in the same direction. The results thus far are preliminary, and the exact mechanism has yet to be established. Madan Biswal has nearly completed his studies of heat treated glassy carbon.

6. RESEARCH PLANS FOR CALENDAR YEAR 1973

Robert H. Bragg

Completion of the work on the graphitization of glassy carbon is expected by the end of the spring quarter. Also, it is expected that the low temperature facility will be in operation by the end of the winter quarter and the experimental work on the low temperature electronic properties of glassy carbon and other materials including extremely high purity Ge can begin. Material available from the solidification studies will also be studied at low temperatures, where unusual changes in conductivity are expected. Work on the acousto-electric effect in pyrolytic graphite will be extended, and studies of the electron-wind effect in Al-CuAl₂ eutectics will be initiated. The Al-Si eutectic appears from the phase diagram to be relatively simple to grow and should have interesting electronic properties, and experiments on the growth and electronic properties of this material will be initiated.

7. 1972 PUBLICATIONS AND REPORTS

Robert H. Bragg and Associates

Published paper

1. F. M. Hamzeh, Formation and Destruction

of Magnetic Islands in Torroidal Systems,
(LBL-1143, October 1972) Phys. Rev. Letters
29, 1492 (1972).

LBL reports

1. F. M. Hamzeh and R. H. Bragg, Small Angle Scattering of X-rays from Oriented Ellipsoids of Revolution, LBL-1176, October 1972.
2. Kwame Ankra, Unidirectional Solidification of Al-CuAl₂ Eutectic (M.S. thesis), LBL-1182, December 1972.
3. M. M. Biswal and R. H. Bragg, Optics of Bonse-Hart Apparatus, LBL-805, February 1972.

III. Ceramic Science

A. HIGH TEMPERATURE REACTIONS

Alan W. Searcy, Principal Investigator

1. THE KINETICS OF VAPORIZATION OF BARIUM SULFATE

Pirooz Mohazzabi and Alan W. Searcy

Equilibrium vapor pressures of barium sulfate and free surface sublimation pressures of (001) face of its single crystals were both measured for the first time from a phase transformation temperature at 1422 to 1540°K, using Torsion-effusion and Torsion-Langmuir techniques, respectively. The reaction was confirmed as

for both equilibrium and free surface conditions. Calculations by the Second Law method yielded, for the reaction,

$$\Delta H_V^0 = 138.9 \pm 1.9 \text{ kcal},$$

$$\Delta S_V^0 = 60.2 \pm 1.3 \text{ eu},$$

for the equilibrium studies, and

$$\Delta H_V^* = 136.4 \pm 2.9 \text{ kcal},$$

$$\Delta S_V^* = 48.0 \pm 2.0 \text{ eu},$$

for the free surface sublimation studies.[†] Thus, within the experimental error,

$$\Delta H_V^* = \Delta H_V^0 \text{ but } \Delta S_V^* < \Delta S_V^0.$$

The rate of the free surface decomposition reaction was constant, within the experimental scatter in data, during the period of the measurements. This result indicates that effusion of the product gases through the porous product layer is not rate limiting even when the product layer thickness is as great as 1 mm. The simplest model consistent with these facts assumes that only 3% of the surface sites are active for the vaporization reaction.

2. THE FRAGMENTATION OF DIMERS OF METAL TRIHALIDES BY ELECTRON IMPACT

Alfred Büchler, James A. Roberts, Jr., and Alan W. Searcy

In the report of their investigation of the vapor over $\text{LaF}_3(\text{s})$ Skinner and Searcy¹ concluded that the monomer/dimer pressure ratios calculated by conventional analysis of their mass spectrometric data were probably too high. They reasoned that this was caused by extensive fragmentation of the dimer molecules under electron impact in the ion source of the mass spectrometer to fragments that were masked by fragments of the monomer molecules, which were present at higher concentrations. The same possibility was raised in the analysis of data subsequently gathered on the vapor over $\text{CeF}_3(\text{s})$.²

To gain an indication of whether or not massive fragmentation of these dimers is likely we have examined the fragmentation pattern of the vapor over $\text{AlCl}_3(\text{s})$ at a temperature (350°K) where the dimer is known to be the major species ($\text{PAICl}_3/\text{PAI}_2\text{Cl}_6 < 10^{-3}$).³ The major fragment observed, Al_2Cl_6^+ (analogous fragments were attributed to the dimers in the CeF_3 and LaF_3 work), has an intensity greater than six times that of any other fragment, such as AlCl_2^+ , that could be attributed to the monomer. Thus fragmentation of Al_2Cl_6 to ions that could be masked by the monomer is not a major reaction.

This result does not completely rule out extensive fragmentation for the lanthanide element fluorides, but it does make it less likely, since fragmentation patterns for chemically similar molecules are generally qualitatively similar. The anomalous behavior of La_2F_6 and Ce_2F_6 appears to be due to selective scattering from the beam outside the effusion cell^{2,4}—a previously unrecognized source of error in mass spectrometer studies. With the source of error identified, the monomer/dimer pressure ratios for the LaF_3 and CeF_3 systems can be calculated by conventional means.

[†] ΔH_V^0 , ΔS_V^0 are the standard enthalpy and entropy for the equilibrium reaction while ΔH_V^* , ΔS_V^* are called the apparent activation enthalpy and entropy for the vaporization reaction.

1. H. B. Skinner and A. W. Searcy, *J. Phys. Chem.* **75**, 108 (1971).

2. J. A. Roberts, Jr. and A. W. Searcy, *High Temp. Sci.* **4**, 411 (1972).

3. JANAF Thermochemical Tables, 2nd ed. NSRDS-NBS 37 (1971).

4. D. J. Meschi, *J. Phys. Chem.* **76**, 2947 (1972). See following abstract.

3. THE MECHANISM OF ZnO SINGLE-CRYSTAL VAPORIZATION

Peter P. Bihuniak, David J. Meschi and Alan W. Searcy

The relative abundance of vapor species from the reaction $\text{ZnO(s)} + \text{Zn(g)} + 1/2 \text{O}_2\text{(g)}$ in their ground and first excited electronic states were compared for equilibrium conditions at 1485°K and Langmuir free surface vaporization conditions at 1640°K by measuring deflections of vapor beams in an inhomogeneous magnetic field. The fractional occupancy of zinc atoms in the first excited 3P state was found to be approximately the same under both Knudsen and Langmuir vaporization conditions. It was not possible to obtain meaningful results for the oxygen vapor because the oxygen background in the system was too high.

4. SCATTERING IN A MOLECULAR BEAM AS A RESULT OF INTRABEAM COLLISIONS¹

David J. Meschi

Collisions between molecules in a molecular beam cause scattering which results in a significant attenuation of the beam intensity in some cases. By the use of a simple model an expression can be derived for S_{AB} , the fraction of A molecules that will traverse the beam without sustaining collisions with B molecules:

$$S_{AB} = \exp \left[- \frac{P_B}{ZKT} \pi \sigma_{AB}^2 \Phi_{AB} (a/\pi)^{1/2} \right]. \quad (1)$$

Here p_B is the partial pressure of B molecules in the source, σ_{AB} is the collision radius for an A-B collision, a is the area of the orifice, and k and T have their usual meaning of the Boltzmann constant and temperature respectively. The quantity Φ_{AB} is the value of $|\vec{v}_A - \vec{v}_B|/v_A$ averaged over the B molecules in the beam and the A molecules passing through the beam. The beam length is assumed to be much greater than $(a/\pi)^{1/2}$.

An exact value for Φ_{AB} would be extremely difficult to obtain because of the non-isotropic nature of a beam, but it can be approximated by the expression

$$\Phi_{AB} \approx 2(1 + \mu_{AB})^{1/2} - \frac{\mu_{AB}}{(1 + \mu_{AB})^{3/2}} - 1 - \mu_{AB}^{1/2}, \quad (2)$$

where μ_{AB} is the ratio of molecular weights M_A/M_B . This approximation results in too low a value for Φ_{AB} , so that its substitution in Eq. (1) gives an upper limit for S_{AB} .

Application of Eq. (1) to typical examples taken from high temperature mass spectroscopy² reveals that at high source pressures an appreciable fraction of some species may be lost from the beam—as much as a third in one example.² The fraction lost will vary with the species because of the parameters p_B , σ_{AB} , and Φ_{AB} . In general, larger molecules and minor species tend to be scattered most.

1. D. J. Meschi, J. Phys. Chem. **76**, 2947 (1972).

2. J. A. Roberts, Jr., and A. W. Searcy, High Temp. Sci. **4**, 411 (1972).

5. GASEOUS THALLIUM (I) METABORATE AND THALLIUM (I) ALUMINUM FLUORIDE

Alfred Blichler and David H. Feather

While all the thallium (I) halides have been studied, only two gaseous ternary compounds of monovalent thallium, thallium (I) nitrate and thallium (I) sulfate, have been studied so far. The purpose of this work was to extend the range of known gaseous ternary compounds of thallium (I) and to compare their mass spectrometric behavior to that of the corresponding alkali compounds.

The vapors above thallium (I) metaborate and a equimolar mixture of thallium (I) fluoride and aluminum fluoride were examined in an Atlas CH-4 mass spectrometer. The mass spectrum of thallium (I) metaborate is similar to that of the alkali metaborates. Both thallium (I) metaborate monomer, TlBO_2 , and dimer, $\text{Tl}_2(\text{BO}_2)_2$, are present in the vapor, the latter identified by means of the fragment ion Tl_2BO_2^+ . The dimer parent ion $\text{Tl}_2(\text{BO}_2)_2^+$ was not found; it was present to the extent of less than 1 part in 400 of the fragment ion Tl_2BO_2^+ . For gaseous thallium (I) nitrate dimer the fragment ion, Tl_2NO_3^+ , was also the only ion observed. In this respect the two thallium pseudohalides differ from the thallium halides, which, in contrast to the alkali halides and pseudohalides, contain parent dimer ions in their mass spectra.

In the vapor above the $\text{TlF} - \text{AlF}_3$ mixture, the mixed thallium (I) aluminum fluoride, TlAlF_4 , is present. In addition the presence

of the ion $Tl_2AlF_4^+$ shows the existence of a higher polymer. In analogy with the assignment of the corresponding ions in the $LiF-AlF_3$ and $NaF-AlF_3$ systems, we are inclined to assign this ion to the double dimer $Tl_2(AlF_4)_2$. In the case of $TlAlF_4$, the parent ion $TlAlF_4^+$ is present in the mass spectrum, in contrast to $LiAlF_4$ and $NaAlF_4$, in whose mass spectra only the fragments $LiAlF_3^+$ and $NaAlF_3^+$ are observed.

The difference in behavior between the two sets of compounds may be explained by reference to recent work on $TlCl$ and $TlBr$, which has shown the highest lying orbital to be a thallium s-orbital.¹ Removal of this s-electron on ionization will actually strengthen the $Tl-X$ ionic bond, the ion formed being effectively Tl^{++X} . Removal of a halogen p-electron removes the charge on the halogen and leads to the fragment ion Tl^+ . This analysis may be extended to $TlAlF_4$ and the alkali aluminum fluorides if we assume that the mixed thallium halide has the same structure as $NaAlF_4$, which has two bridging fluorine atoms between the sodium and aluminum atoms. Removal of a thallium s-electron leads to the parent ion $TlAlF_4^+$, whereas no such process is possible in the alkali compounds. Removal of a bridging fluorine p-electron, on the other hand, leads to the fragment ions $MAIF_3^+$ in both the thallium and alkali compounds.

1. J. Berkowitz, J. Chem. Phys. 56, 2766 (1972); J. Berkowitz and J. L. DeHmer, *ibid.*, 57, 3194 (1972).

6. THE ZEEMAN EFFECT IN Se_2

Alfred Büchler

In consultation with J. T. Hougen (National Bureau of Standards) a scheme for the calculation of the Zeeman effect in Se_2 has been developed. The exact equations for the rotational energy levels for a case between Hund's cases (b) and (c) have been derived and will be used to calculate the unperturbed energy levels for Se_2 . If the spacing of the rotational levels is sufficiently large, a perturbation treatment will then be used to determine the effect of the magnetic field on the energy levels. Magnetic moments for the various rotational states can then be derived by determining the variation of energy with applied magnetic field.

7. THE CONDITIONS OF CHEMICAL EQUILIBRIUM

Alan W. Searcy

Accepted thermodynamic theory assumes chemical equilibrium to require that the chemical potential μ_i of each component i be the same throughout the system. A thermodynamic theory is developed in which a more restrictive constraint is postulated. Each chemical component is assumed to be characterized by an average molar free energy content which must have the same value in each phase of a system at equilibrium. Subsets of a chemical component in non-ideal phases at equilibrium may have different sets of accessible energy states from those available to other subsets; as a consequence, the average molar free energies for a component i of such phases may differ from μ_i when the average molar free energies are equal.

The new theory is consistent with the laws of thermodynamics, and it predicts the same conditions of equilibrium as accepted theory for homogeneous reactions in dilute solutions, even if imperfect, and in heterogeneous equilibria of all components between perfect solutions or of solutes between dilute solutions. But conditions of heterogeneous equilibria involving one or more non-ideal solutions are predicted to be different from conditions predicted by accepted theory.

Inconsistencies which have been reported between values of μ_i calculated from calorimetric data for metallic solutions and values from vapor pressure or emf measurements are predicted by the new theory.

8. THE RELATIONSHIP BETWEEN FORWARD AND REVERSE REACTION RATES UNDER NON-EQUILIBRIUM CONDITIONS

Alan W. Searcy, Alfred Büchler and Dario Beruto

One of the most important questions of reaction kinetics is the circumstance under which the ratio of the rate constants for a forward and reverse reaction can be equated to the equilibrium constant for the reaction in question. But theoretical proof of the relation apparently had been given only for ideal solutions.

It is shown that for a given elementary reaction, and under nonequilibrium conditions, the ratio of the rate constant of the forward reaction to the rate constant of the reverse reaction is the equilibrium constant, as long as both forward and reverse reaction take

place under the same experimental conditions as long as products and reactants establish an equilibrium distribution of states to the transition complex of the reaction.

The proof has an immediate application to vaporization kinetics. As a consequence of the proof it is possible to eliminate one difficult-to-measure variable from an equation that relates pressures measured in effusion studies to the equilibrium vapor pressure of a material inside an effusion chamber. The proof also establishes means for correcting experimental rate data in solution reactions for the effect of the back reaction as equilibrium is approached.

5. RESEARCH PLANS FOR CALENDAR YEAR 1973

Alan W. Searcy

Theoretical work on the thermodynamics of solutions and of surfaces and interfaces will be continued.

We plan exploratory mass spectrometer investigation of the feasibility of determination of the changes in composition and partial pressures that occur in order to displace a phase of narrow composition range to its new composition of congruent sublimation after a change in temperature. If the method proves satisfactory we will be able to make direct measurements of the partial molal Gibbs free energies of the phases at equilibrium near their congruent compositions. Comparison of these values with values calculated from directly measured activities of the components in the vapor phase would provide a new experimental test of the thermodynamic theory of heterogeneous equilibrium. The studies might also lead to a convenient method for making small changes in compositions and therefore of electrical properties of semiconductors.

We are completing a paper on the interpretation of the terrace-ledge-sink (t-l-k) model of vaporization of solids in terms of transition state theory. The theories are shown to be complementary, but some formulations of mechanisms in terms of the t-l-k are inconsistent with transition state theory.

We hope to complete the study of the influence of carbon dioxide pressures on calcite decomposition that was initiated in 1971. The study should yield data both on the reaction kinetics and on the heat of formation of a metastable form of calcium oxide that was identified during our calcite kinetics studies.

A study of the thermodynamics of SrSO_4 decomposition will be initiated. No measurements of this reaction have been reported. We hope later to measure the rate of decomposition of SrSO_4 single crystals for comparison with the thermodynamic data. Only two substances, calcite (CaCO_3) and barite (BaSO_4), have been subjected to kinetic studies of the type we plan.

A mass spectrometer study of the kinetics of decomposition of nitric oxide on tungsten and of its reaction with tungsten at high temperatures has been initiated. The study is of interest both because of the importance of oxides of nitrogen in air pollution and because of the insight to heterogeneous reaction kinetics that can be obtained from comparison of the results with earlier measurements of oxygen-tungsten reactions.

If funding permits, we will initiate an attempt to measure by a differential method the changes in vapor pressure of a liquid, probably water, produced when the liquid is in contact with a large area of an active solid surface. According to accepted surface thermodynamic theory, there should be no difference so long as the liquid surface remains plane, but an experimental test has apparently not been made. Funding limitations have forced abandonment of plans to study the details of kinetic energy transfer from hot surfaces to cold gases.

10. 1972 PUBLICATIONS AND REPORTS

Alan W. Searcy and Associates

Journals

1. Alfred Büchler and Alan W. Searcy, The Formation of Vapor Phase Nuclei in Nucleate Boiling, Monatshefte für Chemie 103, 503 (1972) (article in German). English version, UCRL-20552).
2. James A. Roberts, Jr., and Alan W. Searcy, The Stabilities of $\text{Ce}_2\text{F}_6(\text{g})$ and $\text{La}_2\text{F}_6(\text{g})$, High Temp. Sci. 4 [5], 411 (1972).
3. David H. Feather, Alfred Büchler, and Alan W. Searcy, The Vapor Pressures of Gallium Trifluoride Monomer and Dimer, High Temp. Sci. 4 [4], 290 (1972).
4. David J. Meschi, Scattering in a Molecular Beam as a Result of Intrabeam Collisions, J. Phys. Chem. 76, 2947 (1972).

LBL reports

1. Alan W. Searcy, The Conditions of Chemical Equilibrium, LBL-898, July 1972.

2. Harry B. Skinner and Alan W. Searcy, Mass Spectrometric Studies of Gaseous Oxides of Rhenium, LBL-1139, October 1972.

3. Roy Tom Coyle, Vaporization Kinetics of Magnesium Nitride (Ph.D. thesis), LBL-136, January 1972.

4. Peter P. Bihuniak, The Mechanism of ZnO Single Crystal Vaporization, (M.S. thesis), LBL-867, June 1972.

5. David Hoover Feather, Mass Spectrometric Studies of Inorganic Vapors (Ph.D. thesis), LBL-844, September 1972.

6. Pirooz Mohazzabi, The Kinetics of Vaporization of Barium Sulfate, (M.S. thesis), LBL-1416, December 1972.

B. MICROSTRUCTURE AND BEHAVIOR OF CERAMIC MATERIALS: GLASS AND CERAMIC-METAL SYSTEMS

Joseph A. Pask, Principal Investigator

A continuing overall objective of the research program is to contribute to the development of a fundamental understanding of the factors involved in obtaining ceramic materials with controlled character (which includes microstructure), and of the relationship of character to mechanical behavior at room and high temperatures. This objective involves studies on the kinetics and mechanisms of solid state reactions which in general play a part in the development of microstructure. It also 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.

A second objective of this program is concerned with structural, thermodynamic, and electrochemical studies of glass, 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.

1. STABLE AND METASTABLE EQUILIBRIA IN THE SILICA-ALUMINA SYSTEM

Ilhan A. Aksay and Joseph A. Pask

Sapphire-fused silica diffusion couples annealed in sealed Mo crucibles in the temperature range of 1678 to 2003°C were analyzed by electron beam microprobe. Interfacial compositions across the phase boundaries were used to determine the stable composition range of the mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) phase field, ranging from 70.5 to 74.0 wt % Al_2O_3 , and the alumina liquidus (Fig. 1). Incongruent melting of mullite as determined by Bowen and Greig³ was confirmed. Quenching of melts by using sealed Mo crucibles also confirmed the incongruent melting of mullite. However, metastable extension of the mullite field above its peritectic temperature and the metastable solidification of mullite with alumina contents up to 83 wt % were easily realized.

1. R. F. Davis and J. A. Pask, Diffusion and Reaction Studies in the System $\text{Al}_2\text{O}_3\text{-SiO}_2$, *J. Am. Ceram. Soc.* **55** [10], 525-531 (1972).

2. J. F. MacDowell and G. H. Beall, Immiscibility and Crystallization in $\text{Al}_2\text{O}_3\text{-SiO}_2$ Glasses, *J. Am. Ceram. Soc.* **52** [1], 17-25 (1969).
3. N. L. Bowen and J. W. Greig, The System: $\text{Al}_2\text{O}_3\text{-SiO}_2$, *J. Am. Ceram. Soc.* **7** [4], 238-254 and [5], 410 (1924).

Fig. 1. $\text{SiO}_2\text{-Al}_2\text{O}_3$ equilibrium phase diagram as determined from the interfacial compositions of sapphire-fused silica diffusion couples. Mullite liquidus is by Davis and Pask.¹ Metastable immiscibility and spinodal regions are by MacDowell and Beall.²

(XBL 729-7039)

2. DIFFUSION AND REACTION STUDIES IN THE SYSTEM $\text{Al}_2\text{O}_3\text{-SiO}_2$

Robert F. Davis[†] and Joseph A. Pask

High-temperature diffusion kinetics and phase relations between couples of fused SiO_2 or cristobalite and sapphire or mullite were investigated in air and in helium. Subsolidus liquid formation between sapphire and cristobalite indicates the existence of a metastable system without mullite. A liquid phase is considered to be essential for the nucleation of mullite. The growth rate of mullite exceeded its dissolution rate in

semi-infinite fused-SiO₂-sapphire couples above 1634°C. The interfacial liquid compositions provided data for a minor revision of the mullite liquidus curve. Diffusion coefficients calculated from the Al profiles vary greatly with concentration and temperature, resulting in a large range of values for apparent activation energy, which decreases with increasing Al₂O₃ content (≈ 310 to ≈ 60 kcal/mol for ≈ 4 to ≈ 22 wt % Al₂O₃). The diffusion process in the liquid is considered to be cooperative movement of oxygen-containing Al and Si complexes whose nature changes with composition and temperature; this change in the diffusing species contributes to the range in the values of experimental apparent activation energies.

* Abstracted from J. Am. Ceram. Soc. 55 [10], 525-531 (1972).

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3. DIFFUSION STUDIES IN THE SiO₂-Al₂O₃ SYSTEM IN THE TEMPERATURE RANGE OF 1800 TO 2000°C

Ilhan A. Aksay and Joseph A. Pask

Boltzmann-Matano analysis was used to analyze the diffusion profiles of the sapphire-fused silica couples annealed in the temperature range of 1803 to 2003°C. The diffusivities of aluminum cation in aluminum-silicate melts were concentration dependent and varied by three orders of magnitude at a given

Fig. 1. Computer-determined diffusivity of aluminum ion vs concentration in aluminum-silicate melts in the temperature range of 1803 to 2003°C. (XBL 729-7040)

Fig. 2. The variation of activation energy with concentration for aluminum ion diffusion and viscous flow^{1,2} in SiO₂-Al₂O₃ melts. The diffusion data below 1870°C are by Davis and Pask.³ (XBL 729-7038)

temperature (Fig. 1). The activation energy for diffusion obtained from these data decreases from 211.1 kcal/mol to ≈ 40 kcal/mol with increasing alumina content of the melt (Fig. 2). An analogous relationship also exists between the activation energy for viscous flow and the alumina content of the melt.^{1,2} The diffusion mechanism of low alumina contents is believed to be a cooperative movement of large oxygen-containing aluminum and silicon complexes in a type of ring mechanism. The size of the aluminum-containing diffusing units decreases gradually with increasing alumina content up to ≈ 40 mol % Al₂O₃. Above this concentration, structural changes cease with the complete breakdown of the silica network.

1. R. Rossin, J. Bersan, and G. Urbain, Viscosity of Fused Silica and Slags Belonging to the $\text{SiO}_2\text{-Al}_2\text{O}_3$ System, *Compt. Rend. Acad. Sci. Paris* **258** [2], 562-564 (1964).
2. B. S. Mitin and Yu. A. Nagibin, Viscosity of $\text{Al}_2\text{O}_3\text{-SiO}_2$ Melts, *Izv. Vyssh. Ucheb. Zaved., Chern. Met.* **12** [7], 8-10 (1969) (Russian). UCRL-Trans-1479, July 1972.
3. R. F. Davis and J. A. Pask, Diffusion and Reaction Studies in the System $\text{Al}_2\text{O}_3\text{-SiO}_2$, *J. Am. Ceram. Soc.* **55** [10], 525-531 (1972).

4. DENSITIES OF $\text{SiO}_2\text{-Al}_2\text{O}_3$ MELTS*

Ilhan A. Aksay, Robert F. Davis,[†] and Joseph A. Pask

An X-radiographic technique developed by Rasmussen and Nelson¹ was used to determine the densities of the $\text{SiO}_2\text{-Al}_2\text{O}_3$ melts in the temperature range of 1700 to 2000°C for the entire binary system. The technique consisted of measuring the volume of a melt at temperature from its radiographed image obtained with a 300 kV X-ray source and relating this volume to its density.

The densities varied linearly with temperature within the temperature range studied. These data were used to determine the variation of the melt densities with alumina content at a given temperature (Fig. 1). In the temperature range of 1800 to 2200°C, the densities increase linearly up to ~4% mol % Al_2O_3 . The negative deviation from linearity at higher alumina contents is indicative of the formation of a "looser" silicate structure. Densities were also calculated by using the partial molar volume data² of Al_2O_3 and SiO_2 which were determined from alkali and alkaline-earth aluminum-silicate densities. The calculated densities are lower than the measured ones (Fig. 1). This discrepancy is explained by the breakdown or opening up of the silicate network when alkali and alkaline-earth oxides are added to silica. Aluminum ions, on the other hand, act as network formers on going into four and/or six-fold coordination. Thus, a higher oxygen density or smaller partial molar volume is realized in the absence of alkali and alkaline-earth metals. The presence of aluminum in four- and six-fold coordination was verified by X-ray spectroscopy.

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1. J. J. Rasmussen and R. P. Nelson, Surface Tension and Density of Molten Al_2O_3 , *J. Am. Ceram. Soc.* **54** [8], 398-401 (1971).
2. Y. Bottinga and D. F. Weill, Densities of Liquid Silicate Systems Calculated from Partial Molar Volumes of Oxide Components, *Am. J. Science* **269** [2], 169-182 (1970).

Fig. 1. Densities of $\text{SiO}_2\text{-Al}_2\text{O}_3$ melts vs mol % Al_2O_3 in the temperature range of 1800 to 2200°C. The data points illustrated with solid triangles are calculated densities at 1900°C based on the partial molar volume data of Bottinga and Weill.² (XBL 729-7036)

* Presented at the 25th Pacific Coast Regional Meeting of the Am. Ceram. Soc., Oct. 25, 1972, Portland, Ore.

5. PERMEATION OF SILICATE LIQUIDS INTO SINTERED MAGNESIA COMPACTS*

Boon Wong and Joseph A. Pask

Fundamentals of permeation kinetics of a liquid into a porous solid compact and the corresponding microstructure changes in the solid due to the permeating liquid, either in the presence or absence of reactions, were studied from both theoretical and experimental viewpoints.

Equations for capillary penetration were developed based on Poiseuille's law for capillary flow and the generalized thermodynamic concept of wetting of a solid by a liquid. A dihedral angle equation used for describing phase distribution (microstructure) in a solid-liquid system was thermodynamically derived and generalized.

Experimental studies were performed on the permeation of a number of silicate liquids into sintered magnesia (MgO) compacts of about 92.5% theoretical density. The experimental results support the theoretical predictions.

Permeation rate of a viscous liquid into a "homogeneous" compact with fine capillaries depends mainly on the driving force for wetting, which in turn depends markedly on the presence and rate of any interfacial chemical reactions. In addition, the average permeation distance of the viscous liquid into the compact increases parabolically with time during the initial stages. A negative deviation from this parabolic relationship usually results at later stages when the back-pressure developed by compression of entrapped gases becomes significant.

The microstructure of a relatively dense solid compact is markedly affected by a permeating liquid. The degree of material redistribution in the solid by a solution-precipitation process is significantly dependent on the degree of reactivity of the liquid with the solid.

* Presented at the 25th Pacific Coast Regional Meeting of the Am. Ceram. Soc., Oct. 25, 1972, Portland, Oregon. Abstracted from LBL-877, August 1972.

6. POLYCRYSTALLINE SPINEL FROM POWDERS PREPARED BY FREEZE DRYING TECHNIQUE*

Chi-Shine Tao and Joseph A. Pask

Stoichiometric spinel ($MgAl_2O_4$) powder was

prepared by calcining freeze dried powders formed from an aqueous solution of magnesium sulfate hydrate and aluminum sulfate hydrate.

The freeze dried powder was characterized by X-ray diffraction analysis, size distribution analysis, and scanning electron microscopy. Thermal reactions of the freeze dried powder were studied by using differential thermal analysis, thermogravimetric analysis, and X-ray diffraction. The formation of spinel was postulated to be an aluminum sulfate decomposition activated reaction. These postulated reactions were verified by calculations of their free energy change. Freeze dried powders were calcined isothermally for one hour at temperatures from 900 to 1400°C. Above 1200°C, a much faster spinel crystallite growth was observed, indicating two different growth mechanisms were operating below and above 1200°C (Fig. 1). The same freeze dried powders calcined at 1000 and 1300°C for 0.2 to 12 hours showed that the spinel crystallite size increased very slowly after 2 hours of calcination.

The reactivity of the freeze dried powder to form spinel on calcination depended upon the freeze drying temperature and the starting solution concentration. Freeze dried powder prepared from a starting solution containing

Fig. 1. Spinel crystallite size vs. calcination temperature. (XBL 7210-7060)

12% by weight of anhydrous magnesium and aluminum sulfates and dried at 25°C was found to be the most satisfactory.

Spinel powders developed from the freeze drying technique consisted of submicron size powders and large aggregates of 5 to 50 microns in size. Large aggregates among the fine powders form regions of lower green density resulting in the formation of a nonhomogeneous sintered microstructure. The factors leading to the formation of large aggregates are being investigated.

* Presented at the 25th Pacific Coast Regional Meeting of the Am. Ceram. Soc., Oct. 25, 1972, Portland, Oregon. Partially abstracted from LBL-876.

7. LIQUID PHASE SINTERING STUDIES*

Carl E. Hoge and Joseph A. Pask

Equations have been derived describing kinetic changes during densification of a sintering powder compact in the presence of a liquid phase. The models used correspond to uniform sized spherical particles forming the solid phase in simple cubic packing. The liquid phase is assumed to wet the solid, and some solid solubility occurs in the liquid. Cases treated include:

1. Small amounts of liquid phase with zero dihedral angle.
2. Large amounts of liquid phase with zero dihedral angle and no gas entrapment.
3. Large amounts of liquid phase with zero dihedral angle and entrapped gases.
4. Small amounts of liquid with nonzero dihedral angle.

Zero dihedral angle cases correspond to sintering by solution-precipitation. With systems having nonzero dihedral angles, the sintering mechanism is solid state, having enhanced vacancy concentration gradients in the solid due to the presence of the liquid. A thermodynamic treatment to determine possible end-point densities in compacts indicates that as the dihedral angle decreases, critical end-point densities exist. Mechanisms of grain growth are also being investigated by using thermodynamic arguments.

Kinetic data is being obtained by using a dilatometric technique. Powder compacts, closely approximating the parameters of the models proposed, are employed to compare densification kinetics with predicted results.

* Partly presented at the 25th Pacific Coast Regional Meeting of the Am. Ceram. Soc., Oct. 25, 1972, Portland, Oregon.

8. IMPACT FRACTURE OF BRITTLE TRANSPARENT MATERIALS

William E. Snowden and Joseph A. Pask

An investigation of the interaction of stress waves with cracks in transparent materials, primarily glass, has continued. An experimental setup consisting of a lens Schlieren system, high speed cameras, a spark-discharge light source, and a magnetic hammer for producing impacts has been investigated for suitability in studying the problem. Several problems related to synchronization of all phases of the event have been solved; in particular, the internal light system of the Beckman and Whitley Model 222 framing camera has been replaced by a small laser, permitting timing pulses for each frame to be recorded.

Flyer straps of several metals were made for use with the magnetic hammer. Aluminum was found to be most suitable, and varying strap thicknesses are being used to give changes in the duration of the impact from approximately 100 nsec to 1 usec. An extensive investigation of flyer characteristics has been undertaken. Streaking camera records are being used to give the velocity-time-displacement history as a function of capacitor bank voltage. The data are useful for determining the experimental conditions necessary to produce an impact of known amplitude and duration occurring at some reproducible time.

A critical review of several theoretical approaches to the problem of crack stability in brittle materials subjected to impact indicates that none of these adequately describes the phenomena. It is easily shown, however, that fracture occurring as a result of stress waves must depend on the existence of both a critical pulse amplitude and a critical pulse duration. The relation between pulse characteristics and crack length is being determined.

9. MECHANICAL BEHAVIOR OF MgO SINGLE CRYSTALS

Chung Dokko and Joseph A. Pask

The effort toward studying the alloying effect on the mechanical behavior of MgO was

discontinued because of the difficulty encountered in obtaining the desired single-crystal specimens. Attention has been directed to the high temperature deformation of MgO single crystals. Specimens may be deformed under increasing or constant stress levels which give rise to stress-strain and creep curves, respectively. It is known that substantially different stress-strain behavior is exhibited, depending on the crystal orientation and hence the operative slip planes. Also, recent work on LiF single crystals of $\langle 100 \rangle$ and $\langle 111 \rangle$ orientation has revealed some differences in creep behavior in terms of primary region, stress dependence of steady-state creep rate, and substructure.¹

In the present study, an attempt is being made to correlate stress-strain and creep behavior in MgO single crystals with different orientations tested over the temperature range of $0.4-0.6 T_m$. Stress-strain curves will be obtained by using both constant stress and constant strain rate conditions. Factors of interest are the observed maximum strain hardening rate at 1000°C , and the contribution of (partial) recovery to the stress-strain behavior. Also, preliminary investigations have repeatedly shown the presence of nonpropagating cracks in the deformed specimen. The effect of such occurrences together with buckling on stress-strain curves will be examined.

In the analysis of creep, points of interest are whether measurable creep occurs in a single crystal at a stress level below the yield stress, and the reason for the long primary region for $\langle 100 \rangle$ crystals compared with $\langle 111 \rangle$ crystals.

1. D. R. Cropper and Joseph A. Pask, Creep of Lithium Fluoride Single Crystals at Elevated Temperatures, LBL-1152, October 1972.

10. EFFECT OF GRAIN BOUNDARY CHARACTER ON HIGH TEMPERATURE MECHANICAL BEHAVIOR OF POLYCRYSTALLINE MgO

William E. Snowden and Joseph A. Pask

The high temperature mechanical behavior of two types of polycrystalline MgO was studied in compression over the temperature range $1200-1400^\circ\text{C}$. Differences in behavior between hot-pressed specimens (Type HP) and specimens which were hot-pressed and annealed (Type HPA) were attributed to differences in the structures of the grain boundary regions. The presence of a grain boundary defect struc-

ture in the specimens of Type HP was found to increase the yield stress and limit the total strain at fracture, presumably by restricting the initiation and propagation of dislocations. In the specimens of Type HPA, lower yield stresses in agreement with values for slip in single crystals and greater plastic strains were observed, indicating that dislocation mobility in polycrystalline MgO is significantly enhanced by annealing out defects along grain boundaries.

Creep results for tests conducted at 1200°C were in accord with the stress-strain observations noted above. For specimens of both types, the experimental values for strain rate $\dot{\epsilon}$ as a function of stress σ were compared with predictions arising from a number of theoretical models. Both experimental data and theoretical predictions for specimens of Type HP are presented in Fig. 1. Creep in this material was found to be controlled by a grain boundary sliding mechanism; the predicted and experimental values for $\dot{\epsilon}$ differ by less than an order of magnitude, and the measured stress exponent $n = 1.8$ is in good agreement with the predicted value

Fig. 1. Experimental data and theoretical predictions for hot-pressed specimens (Type HP). (XBL 727-6602)

Fig. 2. Experimental data and theoretical predictions for hot-pressed and annealed specimens (Type HPA). (XBL 727-6601)

$n = 2$. For the specimens of Type HPA, experimental data and predictions arising from the Weertman dislocation glide and climb model are presented in Fig. 2. Creep in this material was found to be controlled by a dislocation climb mechanism, and a stress exponent $n = 7$ was measured. While this value is higher than $n = 4.5$ predicted by the Weertman model, this dependency is sensitive to dislocation density and breaks down at some critical stress σ^* . For the specimens of Type HPA, σ^* was found to be approximately equal to the lowest stress (10,000 psi) used in this work. Thus the value $n = 7$ determined experimentally is found to be consistent with the Weertman model in the regime where an exponential relation between $\dot{\epsilon}$ and σ is predicted.

The apparent activation energy Q for creep was determined by using an incremental temperature technique. For specimens of Type HP, a value for Q of ~ 70 kcal/mol was found, while for specimens of Type HPA a value of

~ 110 kcal/mol was observed. These values are in agreement with previously reported values for the activation energies for extrinsic and intrinsic diffusion of oxygen, respectively.

11. CONTROL OF GRAIN BOUNDARY CHARACTER IN POLYCRYSTALLINE MgO

Truett Sweeting and Joseph A. Pask

The nature of the grain boundary has been found to be significant in controlling the mechanical behavior of polycrystalline MgO.¹⁻³ Factors that determine the grain boundary structure in processing are being studied. Resulting microstructures are being analyzed with emphasis on grain boundary nature. Stress-strain tests will be made to relate the resulting structures to mechanical behavior.

1. S. M. Copley and J. A. Pask, Deformation of Polycrystalline MgO at Elevated Temperatures, J. Am. Ceram. Soc. 48 [12], 636-642 (1965).
2. T. G. Langdon and J. A. Pask, Effect of Microstructure on Deformation of Polycrystalline MgO, J. Am. Ceram. Soc. 54 [5], 240-246 (1971).
3. W. E. Snowden, High Temperature Mechanical Behavior of MgO-CaO-MgO-SiO₂ Materials (M.S. thesis), UCRL-20567, July 1971.

12. INTERFACIAL REACTIONS AND WETTING BEHAVIOR OF GLASS-IRON SYSTEMS*

Carl E. Hoge, John Brennan,[†] and Joseph A. Pask

Interfacial reactions and enhanced wetting or spreading of Na₂Fe₃Si₂O_{5+x} and Na_{2-2x}Fe_xSi₂O₅ glasses on substrate of high purity iron (Marz) and commercial iron (Armco) were observed at 1000°C at low partial pressures of O₂ and Na vapors. Reactivity increased with increase of the oxygen/silicon ratio in the glass and purity of iron, and with decrease of the gas pressures.

* Abstracted from LBL-480, July 1972.

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13. EFFECT OF COMPOSITIONS ON GLASS-METAL INTERFACE REACTIONS AND ADHERENCE*

John Brennan† and Joseph A. Pask

Reduction-oxidation reactions and enhanced wetting or spreading of $\text{Na}_2\text{Fe}_x\text{Si}_2\text{O}_5+x$, $\text{Na}_2\text{Co}_x\text{Si}_2\text{O}_5+x$, and $\text{Na}_2\text{Ni}_x\text{Si}_2\text{O}_5+x$ glasses on substrates of Fe, Co, Ni, NiFe, and NiCo were observed at 1000°C at low partial pressures of O_2 and Na vapors as the O/Si ratio of the glass was increased. When the substrate metal had a higher oxidation potential than the metal of one of the cations in the glass, e.g., CoO containing glass on Fe, redox reactions resulted in the formation of metallic precipitates under all conditions. A third type of redox reaction based on reduction of the valence of a cation in the glass, e.g., Fe^{3+} to Fe^{2+} , also occurred. Adherence developed between substrates and glasses containing amounts of substrate oxide approaching saturation either in the starting composition or attained by redox reactions.

*Abstracted from LBL-481, July 1972.

†Present address: United Aircraft Research Labs., East Hartford, Conn. 06108.

14. ELECTROCHEMICAL STUDIES OF THE $\text{FeO}_{.95}\text{O}-\text{Na}_2\text{O}-\text{SiO}_2$ GLASS SYSTEM

Robert B. Langston and Joseph A. Pask

Glass specimens of several ternary compositions have been prepared in preparation for galvanic cell measurements at temperatures of 700 to 1030°C. These have been analyzed chemically by using atomic absorption techniques. These experiments will also provide information on the liquidus surface of the ternary phase diagram $\text{FeO}_{.95}\text{O}-\text{Na}_2\text{O}-\text{SiO}_2$.

15. RESEARCH PLANS FOR CALENDAR YEAR 1973

Joseph A. Pask

a. Solid State Reactions

Diffusion experiments designed to determine the chemical interdiffusion kinetics of aluminum and silicon ions in mullite are continuing. The effect of solid solution additives to mullite on diffusion kinetics will also be determined.

Studies will also be undertaken on the mechanisms and kinetics of interdiffusion and moving boundaries in single crystal oxide couples. Diffusion data will be interpreted in terms of thermodynamic properties of the system.

b. Development of Microstructures

Studies of the factors that play a role in liquid phase sintering and in the development of microstructure are continuing. The approach will consist of selecting systems in which a range of dihedral angles will exist. Thermodynamic, as well as kinetic, arguments will be applied.

Freeze drying techniques are continuing to be utilized in the preparation of powders for purposes of attaining polycrystalline materials with controlled composition and microstructure. Particular attention will be paid to the optimization of the process to prevent the formation of aggregates, or to break them up easily, in order to realize a completely uniform texture in the compacted powders.

c. Mechanical Behavior

An investigation of crack propagation in brittle transparent materials subjected to high velocity impacts is continuing. The phenomenon of branching in a brittle material subjected to transient stresses will also be investigated.

Stress-strain and creep data will be obtained at high temperatures on MgO single crystals. These will be correlated for purposes of evaluating deformation mechanisms and the conditions under which internal cracks form.

The stress-strain behavior of polycrystalline MgO specimens with different grain boundary characteristics will be evaluated. Specimens will be prepared with the nature of the grain boundary as a variable. Some stress-strain data will also be obtained on polycrystalline spinel.

d. Glass Studies

Determinations of activities of iron oxides in sodium silicate glasses by electrochemical methods, and calculations of thermodynamic properties are being continued. Associated information will assist in checking the $\text{FeO}-\text{Na}_2\text{O}-\text{SiO}_2$ phase diagram.

16. 1972 PUBLICATIONS AND REPORTS

Joseph A. Pask and Associates

Journals and books

1. Robert F. Davis, İlhan A. Aksay, and Joseph A. Pask, Decomposition of Mullite, J. Am. Ceram. Soc. 55 [2], 98-101 (1972) (UCRL-20536).
2. Joseph A. Pask, Chemical Reactions and Adherence at Glass-Metal Interfaces, in Proceedings of the Porcelain Enamel Institute (Technical Forum 1971), 33, 1-16 (1972) (LBL-166).
3. Robert F. Davis and Joseph A. Pask, Diffusion and Reaction Studies in the System $Al_2O_3-SiO_2$, J. Am. Ceram. Soc. 55 [10], 525-531 (1972) (UCRL-19644 Rev. 2).

Invited papers presented

1. "Metal-Ceramic Bonding," A.I.M.E. No. Calif. Metallurgical Section Symposium on Joining of Materials, Palo Alto, March 18, 1972.
2. Chairman, U.S.-Japan Seminar on Basic Science of Ceramics, "Equilibria and Kinetics in Modern Ceramic Processing," Berkeley, April 28; Niagara Falls, N.Y., May 1; Penn State Univ., May 3-5, 1972.
3. "Nature of Glass-Metal Interfaces," Symposium on Interfacial Bonding and Fracture in Polymeric, Metallic and Ceramic Composites, U.C.L.A., Los Angeles, Calif., Nov. 13-15, 1972.

LBL reports

1. C. E. Hoge, J. Brennan, and J. A. Pask, Interfacial Reactions and Wetting Behavior of Glass-Iron Systems, LBL-480, July 1972.
2. J. Brennan and J. A. Pask, Effect of Compositions on Glass-Metal Interface Reactions and Adherence, LBL-481, July 1972.
3. C. C. Tao, Polycrystalline Spinel from Powders Prepared by Freeze Drying Technique (M.S. thesis), LBL-876, June 1972.
4. B. Wong, Permeation of Silicate Liquids into Sintered Magnesia Compacts (M.S. thesis), LBL-877, August 1972.
5. W. E. Snowden and J. A. Pask, Effect of Grain Boundary Character on High Temperature Mechanical Behavior of Polycrystalline MgO , LBL-1120, December 1972.
6. D. R. Cropper and J. A. Pask, Creep of Lithium Fluoride Single Crystals at Elevated Temperatures, LBL-1152, September 1972.
7. Abbaraju P. Raju, İlhan A. Aksay, and Joseph A. Pask, Permeation of Silicates in Magnesia and Forsterite Compacts, LBL-159 Rev., May 1972.

C. RELATION OF MICROSTRUCTURE TO PROPERTIES IN CERAMICS

Richard M. Fulrath, Principal Investigator

1. HOT STAGE SEM STUDIES OF THE INITIAL STAGE SINTERING OF COPPER AND NICKEL*

Craig B. Shumaker†

In the past, experimental procedures for studying isothermal sintering have used dilatometers to measure shrinkage of compacts, electron images to measure neck growth and the length change of lines of spheres, and the hot stage optical microscope to measure neck growth and two-sphere shrinkage. The recent developments in scanning electron microscopy by Fulrath¹ have allowed continuous observation of the sintering phenomena at temperatures up to 1600°C with magnifications from 50 to 5000×

Initial work on the first stage sintering of copper and nickel microsphere compacts using data obtained from the SEM is completed. Shrinkage measurements were made from photographs of the compact surface taken from the SEM television monitor at low magnification.

Isothermal sintering experiments have shown that considerable erratic linear change occurs before continual shrinkage commences. Figure 1 shows typical sintering behavior of a ~30×20 μm nickel sphere compact of 43% green density. The $\Delta L/L_0$ calculations, linear least square slopes, graphs and time-length corrected data calculations were made by computer analysis.

After time-length corrections to eliminate

Fig. 1. Isothermal sintering of a compact of Ni microspheres (slope = 0.609).

(XBL 727-6664)

Fig. 2. Dimensional changes in heating nickel compacts under identical conditions. Ni-1 was compacted to a green density of 42% TD and Ni-2 was 50% TD. Solid line is the change expected from thermal expansion with no shrinkage and dotted line is a least square slope of the experimental data.

(XBL 727-6669)

erratic initial sintering the shrinkage rate (slope) obtained from eight isothermal sintering experiments do not agree with existing sintering theories. Previous shrinkage theories predict $\Delta L/L_0$ proportional to (time)^{0.31-0.50} depending on diffusion paths to the neck surface. This study placed the time exponent (slope) between 0.60 and 0.70.

By superimposing photographs of $t = 0$ and $t = 200$ minutes permanent particle shifts on

the surface of the compact were observed. By replotting the shrinkage data without the measurements that used locations that shifted permanently, the initial erratic sintering and the need for a time-length correction were avoided. Preselection of data only decreased the standard deviation of the slope; the shrinkage rate itself remained essentially unchanged. However, the error in the average $\Delta L/L_0$ increased at initial times, indicating that even so-called good measuring locations had shifted during the first few minutes of sintering.

The observation of particle rearrangement supports the theory of Exner et al.² that density gradients in real compacts cause non-uniform sintering. Regularly packed volumes are connected by bridges of spheres that have necks of unequal radii of curvature. Mass transport is enhanced on the side of the neck of the smaller radius of curvature causing the bridge (or chain) of spheres to straighten. Hence, uniform shrinkage that occurs in the close-packed regions can be undetected by chain straightening of spheres in adjacent open regions of the compact. It is postulated that sphere to sphere shrinkage theories cannot be applied to real compacts without considering the influence of the initial green density of the compact.

In a preliminary attempt to characterize the effect of green density or initial stage sintering of compacts, two experiments were run using nickel microspheres +20-30 μm with green densities of 42 and 50%. The 42% green dense sample showed nearly no shrinkage despite being at adequate sintering temperature (Fig. 2a), whereas Fig. 2b shows considerable shrinkage for the 50% dense sample using identical experimental conditions. Therefore, it is concluded qualitatively that increased green density reduces the extent of localized sintering.

* Abstracted from C. B. Shumaker, Initial Stage Sintering of Copper and Nickel. (M.S. thesis), LBL-1110, Aug. 1972.

† Present address: Purdue University, Lafayette, Indiana

1. R. M. Fulrath, Scanning Electron Microscopy to 1600°C, in Scanning Electron Microscopy/1972 (Part I), IIR Research Institute, Chicago, April 1972.

2. H. E. Exner, G. Petzow, and P. Wellner, "Problems in the Extension of Sintering

Theories to Real Systems," presented at the Third International Conference on Sintering, Notre Dame University, Indiana, June 1972.

2. SINTERING CERAMIC OXIDES

David N. K. Wang and Richard M. Fulrath

Submicron aluminum oxide particles compacted to nearly 40% TD (theoretical density) have been heated in the hot stage of the scanning electron microscope. The associated sintering, both during heating and while being held at temperature, was determined by the use of markers (tungsten microspheres, +10-20 μm diameter) placed on the compact surfaces.

The specimens were supplied by the General Electric Company, Cleveland, Ohio and consisted of Linde "A" alumina (0.3 μm average particle diameter) doped with 0.1 wt % MgO compacted into disks and prefired to 900°C for one hour to remove organic pressing aids. Specimens for the scanning electron microscope study were small disks 0.25 in. diameter and 0.040 in. thick cut from the original prefired disks.

The heating cycle followed was identical for the two specimens. The samples were first heated to 800°C and held one hour. They were then heated at 4.2°C/min to 1560°C to ensure thermal equilibrium in the hot stage. The samples were then held at 1560°C for 100 minutes.

Figure 1 shows the average linear shrinkage based on 10 measurements at various times in the heating cycle for two specimens. As expected, when 900°C is selected as the initial dimension the compact expands due to thermal expansion until the onset of sintering, which occurs at approximately 1170°C. The shrinkage rate increases until a maximum rate is reached at approximately 1450°C. On further heating and during the isothermal period the rate continuously decreases. The total shrinkage observed and room temperature measurements on the specimen after the sintering run indicate a density increase from approximately 40 to 90% TD.

The data obtained to date on sintering of oxides indicate that the scanning electron microscope will be a powerful tool in studying sintering throughout the whole process.

Fig. 1. Shrinkage characteristics of sub-micron particle Al_2O_3 compacts as determined by hot-stage scanning electron microscopy. Both runs show identical results.

(XBL 731-2049)

3. INTRINSIC AND EXTRINSIC NONSTOICHIOMETRY IN THE LEAD ZIRCONATE-TITANATE SYSTEM[†]

Robert L. Holman[†]

Polycrystalline lead zirconate-titanate (PZT) ceramics are of commercial interest because of their wide range of dielectric constants, pronounced ferroelectric, piezoelectric, and electro-optic behavior, coupled with low cost of processing and manufacture. Several investigators have shown that significant changes in physical properties can result from only slight compositional changes, or deviations in stoichiometry created during processing by the evaporation of lead oxide (PbO). This causes difficulties in the manufacturing of reproducible PZT materials of controlled composition.

Jaffe et al.¹ sought to inhibit this undesirable evaporation of PbO by sintering PZT samples in the presence of the PbO atmosphere provided by lead-oxide-enriched lead zirconate discs. Dungen et al.² used a burial powder of the exact composition as the sample to produce the necessary local equilibrium environment.

Although recent experimenters have been able to obtain improved results using these approaches, stoichiometry variations and inhomogeneities were still observed.

In the present study the range of the intrinsic and the nature of the extrinsic nonstoichiometry in lead zirconate-titanate has been characterized. In addition, a simple method has been developed to allow precise and reproducible control of the defect structure.

Two different gravimetric experiments have led to similar values for the $\text{Pb}(\text{Ti}_x\text{Zr}_{1-x})\text{O}_3$ intrinsic single-phase region width.

a. Vapor Phase Equilibration Experiment

A single-phase, high purity, and porous PZT sample was suspended within a constant activity multi-phase (CAMP) crucible at constant temperature (1100°C) by a wire from a continuously recording microbalance. Weight changes are observed as a consequence of the reaction of the sample with the CAMP crucible atmosphere. When the sample's weight becomes constant, the crucible and the sample will be in a state of quasi-equilibrium.

As an example, the proposed PbO-TiO_2 phase diagram and its corresponding lead oxide isothermal (1100°C) activity diagram is shown in Fig. 1, assuming a small degree of nonstoichiometry. Composition A, high PbO CAMP, refers to a two-phase mixture of PZT with excess PbO . Composition B, low

Fig. 1. (a) Proposed PbO-TiO₂ phase diagram after Moon, and assuming a lead titanate region of nonstoichiometry. (b) Activity of PbO vs. mole fraction PbO at constant temperature (1100°C) for the lead titanate binary. Points A and B designate the constant PbO atmospheres provided by the CAMP crucibles of these compositions; point C locates the composition and activity of the nearly stoichiometric single-phase compound, whereas D and E indicate the single-phase boundaries. (XBL 726-6447)

PbO CAMP, refers to a multi-phase mixture of PZT with excess titania and/or zirconia. Composition C designates the initial stoichiometry of a single-phase sample. The exact location of C is dependant upon the materials's processing history.

The sample, activity C, is first equilibrated with the atmosphere provided by a high CAMP crucible of composition A. The activity difference between the sample and the

crucible, assisted by the high vapor pressure of PbO at temperature, causes the sample to gain weight (PbO) until its activity is raised to equal that within the crucible of PbO activity A. Weight gain will stop at composition point D, fixing one side of the single-phase region. The sample will continue to maintain this weight for as long as the atmosphere within the crucible remains at a constant PbO activity.

Next, this sample, now with PbO activity D, is equilibrated with a low CAMP crucible of composition and PbO activity B. This new PbO activity difference causes the sample to lose weight to the atmosphere, until point E is attained. This point defines the low PbO activity side of the single-phase region. Hence, the weight change (loss), D to E, should exactly correspond to the molar width of the single-phase region.

By replacing the sample at activity E, in the first crucible of high activity A, reversibility may be demonstrated by a weight gain exactly corresponding to the previous weight loss.

b. Knudsen Effusion Experiment

The "vapor phase equilibration" (VPE) experiment measured the width of most PZT single-phase regions while also affording a unique method of fixing the stoichiometry during processing. However, the technique could not be applied as easily to the solid solution compositions at/or quite near pure lead titanate or lead zirconate because of difficulties encountered in fabricating mechanically stable atmosphere crucibles and samples. Hence, another approach was taken.

A variation of the standard Knudsen effusion cell allows for an extended interpretation of the vapor pressure data. In fact, a single experiment may be designed to yield the width of any PZT single-phase region, the equilibrium lead oxide vapor pressure data as a function of temperature and composition, and the exact location of the stoichiometric composition, $Pb(Ti_xZr_{1-x})O_3$, within its single-phase region. This is possible because only a single component, PbO, evaporates, so that the composition of the remaining condensed phase changes uniformly, and can be so constrained to cross the desired phase boundaries at constant temperature.

A typical Knudsen effusion experiment was conducted where the sample is sealed within a non-reacting cell containing a small cylindrical orifice, and the cell is continuously weighed, in vacuum, as a function

of temperature. At constant temperature, the equilibrium vapor pressure builds up within the cell, and the orifice area acts as the effective area from which the vapor molecules will escape at the equilibrium rate. This equilibrium escape rate is inferred from the weight-change of the cell by means of the Knudsen equation

$$p = (dw/dt) [2kT/m]^{1/2} / A_0 W,$$

where p = equilibrium vapor pressure
 dw/dt = the weight-loss-rate of the cell
 T = the temperature of the orifice in degrees Kelvin
 m = mass of the effusing specie (PbO)
 A_0 = the orifice area
 W = the Clausius correction factor for the cylindrical orifice
 k = Boltzman's constant.

The experimental variation instituted in this study consisted of initially preparing a well characterized lead zirconate-titanate plus lead oxide powder sample, continuing the Knudsen effusion experiment until all the lead oxide is exhausted from the cell, and then recording the weight and analyzing the oxide residue.

If the observed rate of weight loss of the cell is constant, so is the PbO equilibrium vapor pressure, and the composition of the sample lies in a two-phase region. When the rate of weight loss is not constant, the equilibrium PbO vapor pressure is changing with time and the sample contains only a single phase. Throughout a two-phase region, the overall sample composition is changing, but the vapor pressure of PbO is not.

When during the course of the experiment the lead oxide effusion causes the sample composition to cross into the PZT single-phase region, the weight-loss rate observed became nonlinear and slower, reflecting the reduced lead oxide activity in the sample as it becomes more deficient with respect to lead. When the continuous effusion of lead oxide causes the appearance of a new second phase the weight-loss rate, and therefore the vapor pressure, will become constant once again. Thus, the amount of lead oxide lost during the nonlinear portion of the weight-loss data will correspond to the exact width of the PZT single-phase region with respect to PbO at that temperature, or the degree of nonstoichiometry of the compound, as is illustrated in general in Fig. 2.

Figure 3 summarizes the entire form of the data. The actual results are summarized in

Fig. 2. General form of the Knudsen effusion data at a constant temperature when the Knudsen sample alters its composition through the $PbTi_{1-x}Zr_xO_3$ single-phase region. This corresponds to the nonlinear portion of the weight-loss vs. time curve. (XBL 726-6445)

TYPICAL WEIGHT LOSS DATA FROM KNUDSEN EFFUSION EXPERIMENT ON $(Pb_{1-x}Zr_x)O_3 + 8PbO$

Fig. 3. Knudsen cell weight loss vs. time during a typical experiment. Equilibration at successive temperatures on both sides of the single-phase region allows efficient collection of vapor pressure data. ΔW , corresponding to the weight-loss from B to C on the activity diagram, measures the width of the PZT single-phase region. (XBL 723-6075A)

Table I where "mol. and wt.%" refers to the percent lost. They agree closely with the data obtained by "vapor phase equilibration" techniques. It is seen that both the terminal compositions, lead titanate and lead zirconate, possess the widest ranges of non-stoichiometry in the system.

Table I. Tabulated results of the "Vapor phase equilibration (VPE)" experiment and the Knudsen Effusion (KE) experiment defining the extent of nonstoichiometry on width of the PZT single-phase region.

y	ΔW SINGLE-PHASE WIDTH			SAMPLE COMPOSITION (BOUNDARY)					EXPERIMENTAL METHOD	
	WT. %	"MOL. % PbO"	x	MOL. % PbO	MOL. % TiO ₂	MOL. % TiO ₂	MOL. % ZrO ₂	MOL. FRACTION PbO	V.P.E.	K.E.
1.0	7.36	10.0±1.0	0.100	45.0	5.0	50.0	0	0.474		X
0.9	4.01	5.5±0.5	0.055	47.25	2.75	45.0	5.0	0.486	X	X
0.8	3.1	4.2±0.5	0.042	47.9	2.1	40.0	10	0.490	X	X
0.65	1.89	2.7±0.3	0.027	48.6	1.35	32.5	17.5	0.493	X	X
0.5	1.72	2.48±0.3	0.025	48.75	1.25	25.0	25.0	0.494	X	X
0.4	1.08	1.6±0.2	0.016	49.2	0.8	20.0	30.0	0.495	X	X
0.2	1.98	3.0±0.5	0.030	48.5	1.5	10.0	40.0	0.4925	X	X
0	6.1	9.5±1.0	0.095	45.475	4.525	0	50.0	0.475		X

FORMULAE USED *

$$(1) \text{ "MOL. \% PbO" } = \frac{\text{NO. MOLES PbO LOST}}{\text{NO. MOLES PbO IN SAMPLE}} (100) = \frac{(\delta W)(\text{MW-PZT})}{223.19 (W_s)} (100)$$

δW = SAMPLE WT. LOSS

$$(2) \text{ "WT. \% PbO" } = \frac{(\text{GRAMS PbO LOST})}{(\text{GRAMS PbO IN SAMPLE})} (100) = \frac{(\delta W) (100)}{[(W_s)/(MW-PZT)] (223.19)}$$

W_s = INIT. SAMPLE WT.

MW-PZT = MOLECULAR WT.

$$\text{ "WT. \% PbO" } = \text{ "MOL. \% PbO" }$$

$$(3) \text{ WT. \% } = \frac{\text{GRAMS LOST}}{\text{SAMPLE WT.}} \times 100 = \frac{\delta W}{W_s} \times 100$$

$$(4) \text{ MOL. \% PbO } = \frac{(1-x)}{2} (100) \quad \text{MOL. \% TiO}_2 = \frac{y}{2} (100)$$

$$\text{MOL. \% TiO}_2 = \frac{x}{2} (100) \quad \text{MOL. \% ZrO}_2 = \frac{(1-y)}{2} (100)$$

$$(5) \text{ MOLE FRACTION PbO } = \frac{1-x}{(1-x)+1} = \frac{1-x}{2-x}$$

*"Mol. or wt % PbO" refers to the percent lost from sample during experiment.

Assuming the rate of weight loss to be proportional to the vapor pressure of PbO within the cell at all times, tangents constructed to the weight-loss curve allow calculation of the lead oxide vapor pressure or activity as a function of composition.

These data, allow the graphical integration of the Gibbs-Duhem equation, which yields the corresponding activity of titania or zirconia and consequently the free energy of mixing as a function of composition through the PZT single-phase region. This calculated free energy of mixing is found to have a minimum within the single-phase region, implying that the stoichiometric composition is not the most stable perovskite. This analysis was applied to both lead titanate and lead zirconate. The reduced experimental results for activity as a function of composition are shown in Fig. 4 for PbTiO_3 . The results of the free energy

of mixings dependence on composition is shown for both materials in Fig. 5.

In addition, each experiment generates lead oxide vapor pressure data for the multi-phase regions that bound the nonstoichiometric compound. The results that are obtained compare favorably with those reported by Hardt and Rau⁵ for the (PZT+Z) phase field.

Because PbO is the only significant vapor species in the $\text{PbO-TiO}_2\text{-ZrO}_2$ system, it is expected that a second law analysis of the Knudsen effusion vapor pressure data should yield equivalent values for the entropies of vaporization. This is observed for PbO, PbTiO_3 , and PbZrO_3 .

By plotting the lead oxide activity of PZT in equilibrium with lead-rich liquid as a function of temperature and the $\text{Pb}(\text{Ti}_x\text{Zr}_{1-x})\text{O}_3$ composition, it is seen that

Fig. 4. Lead oxide and titania activity as a function of composition in the lead titanate single-phase region as determined from analysis of the Knudsen effusion data and a graphical integration of the Gibbs-Duhem equation. (XBL 726-6431)

approximation of PbO activity of PZT plus lead-rich liquid compositions by assuming the applicability of Raoult's law for the liquid phase is invalid. The actual activity coefficients as calculated from the present experimental data, deviate substantially from Raoult's law. (at 1100°C $\gamma_{\text{PbO}} = .28$ for Pb(Ti_{0.5}Zr_{0.5}O₃)

Finally, by evaporation of all the lead oxide from the Knudsen cell, and by carefully weighing and analyzing the sample residue that is left in the cell, it was possible to locate the stoichiometric PZT composition relative to the boundaries of its single-phase region.

By modifying the vapor phase equilibration technique, a third gravimetric experiment could be used to study the kinetics of solution of Bi³⁺, Nb⁵⁺, La³⁺, and Sc³⁺ ions in PZT and thus the extrinsic non-stoichiometry. Results indicated a lead vacancy defect structure created by the substitution of Bi³⁺, Nb⁵⁺, and La³⁺ in the PZT lattice, and an oxygen vacancy defect structure for Sc³⁺, obeying electro-neutrality rules, and following simple predic-

tions of crystal chemistry (Bi³⁺ and La³⁺ substitution for Pb²⁺, Nb⁵⁺ and Sc³⁺ substitution for Ti⁴⁺, Zr⁴⁺).

Small additions of other oxides to PZT will alter its defect structure and have been reported to affect its electrical properties, sintering kinetics, and grain growth. Bismuth and niobium have been shown to act as sintering aids, and to improve the ferroelectric behavior. Lanthanum has markedly enhanced the sinterability of PZT ceramics. Lee⁴ has demonstrated that scandium can convert the ferroelectric characteristics of PZT to an anti-ferroelectric-like behavior.

To generate commercially useful devices, reproducibility of results must be assured, which implies that the processing kinetics must be controlled. It appears that to explain the reported results correctly, one must understand the kinetics of the incorporation of the Bi³⁺, Nb⁵⁺, La³⁺, and Sc³⁺ ions into the perovskite lattice, their location in the lattice, and the defect structure or extrinsic nonstoichiometry that is generated. Consequently, an experiment was developed that provided direct observation of the mechanisms.

Fig. 5. The free energy of mixing PbO and either TiO₂ or ZrO₂ as a function of composition in either the lead titanate or the lead zirconate single-phase region. (XBL 726-6433)

Employment of CAMP PZT crucibles to control atmospheric, thermogravimetry may be used to study the continuous weight changes caused by the reaction between any second phase oxide addition with lead zirconate-titanate. In this analysis, the number of titanium and/or zirconium ions distributed on the B-site of the perovskite lattice is constant due to the extremely low vapor pressure of these species. However, the lead ion concentration is free to adjust itself by means of equilibration with a surrounding lead oxide atmosphere. Hence, should a cation diffuse into the A-sublattice, some lead ions would be released, keeping the ratio of A-sites to B-sites at unity. If a cation diffused into the B-sublattice, the total number of B-sites would be increased, and additional lead ions would be obtained from the atmosphere, again holding the A/B site ratio at unity. This type of reaction weight-change analysis was first demonstrated by Weston et al.,⁵ who determined the substitutional lattice site of Fe^{3+} in lead zirconate-titanate by weighing a sample containing iron oxide before and after a long high temperature firing.

However, this method may be further refined to reveal the valency of the substituted cation and the active charge compensation mechanism. Also, thermogravimetry has the advantage of continuously recording both the weight changes caused by the ionic substitution, including the development of any dominant, though transient, second phases, at the temperature of interest.

Thus, divalent ion substitutions on the A-sublattice and quadrivalent ion substitutions on the B-sublattice of the perovskite require only equivalent amounts of PbO lost or gained from the original composition. However, trivalent ion substitutions on the A-sublattice and pentavalent substitutions on the B-sublattice require an additional mechanism to neutralize the charge imbalance created. This neutralization is assumed to be accomplished by the creation of lead vacancies (reduction in the number of lead ions on lead sites).

If the CAMP crucible is in equilibrium with the PZT sample, all observed weight changes are due to the solution kinetics of the impurity oxides.

Bismuth and Niobium. The samples containing bismuth and niobium were selected as experimental controls. Crystal chemistry considerations present a strong case for assuming that trivalent bismuth will substitute for lead and pentavalent niobium will substitute for titanium/zirconium.

Fig. 6. Continuous weight-change vs. time (hours) at 1150°C of a pre-treated $\text{PbTi}_{1.5}\text{Zr}_{0.5}\text{O}_3$ sample containing 1 mol % lanthanum oxide (La_2O_3): (a) lead oxide atmosphere provided by a stoichiometric $\text{PbTi}_{1.5}\text{Zr}_{0.5}\text{O}_3$ crucible, (b) lead oxide atmosphere provided by a low CAMP crucible (b-dotted) sample contains no binder. (XBL 7010-6820A)

Preliminary experiments⁶ conducted by using a burial powder of the same composition as the sample confirmed this hypothesis.

The present results for 1.0 mol % additions of MO_x to samples of approximately the same weight show weight gains which are significantly larger than reported earlier. This is particularly interesting for the case of Nb_2O_5 substitution. It is suggested that the refractory niobia particles (initially at $\text{app} \approx 0$) react with the lead oxide obtained from the atmosphere (constant $\chi_{\text{PbO}} = 0.280$), forming layers of complex lead niobates as equilibrium conditions are approached. No sample weight losses were observed until the sample had shown a 1.4 wt % gain of PbO. At this point the Nb_2O_5 -PbO phase diagram reveals that the composition is 83 mol % PbO, 17 mol % Nb_2O_5 , which creates about 1.5 vol. % second phase. From the phase diagram it may be seen that at this composition a liquid phase may have formed.

A similar situation is observed in the bismuth modified system, except that the liquid phase forms from the outset (Bi_2O_3 melts at 825°C).

Lanthanum and Scandium. This work was primarily undertaken to investigate the kinetics of solution of the lanthanum and scandium oxides. The reaction weight-change data are presented in Fig. 6(b) and Fig. 7(b) for data representative of 1.0 mol % La_2O_3 and 1.0 mol % Sc_2O_3 respectively.

$$\text{wt \%} = \frac{\text{PbO gain (grams)}}{\text{sample wt (grams)}}$$

Fig. 7. Continuous weight-change vs. time (hours) at 1150°C of a pretreated $\text{PbTi}_{0.5}\text{Zr}_{0.5}\text{O}_3$ sample containing 1 mol % scandium oxide (Sc_2O_3): (a) lead oxide atmosphere provided by a stoichiometric $\text{PbTi}_{0.5}\text{Zr}_{0.5}\text{O}_3$ crucible, (b) lead oxide atmosphere provided by a low CAMP crucible (b-dotted) sample contains no binder. (XBL 7010-6824A)

For the lanthanum substitution, no initial weight gains are observed. However, the rate of equilibration is seen to be quite dependent upon the incorporation of a maximum amount of naphthalene to control porosity. Figure 6(b) demonstrates this effect, where (b-dotted) describes the data of a sample which was sintered simultaneously without naphthalene, and (b-solid) describes the data of an identical sample containing approximately 7 wt % naphthalene. In addition, it was observed that the smaller the sample in volume, the more rapid the equilibration.

In either event, the diffusion of La^{3+} proceeds gradually until an equilibrium is reached corresponding to a total La^{3+} substitution for Pb^{2+} via a total lead vacancy charge compensation mechanism.

Finally, experiments were conducted to characterize the addition of Sc_2O_3 . From crystal chemistry considerations it is deduced that scandium illustrates a trivalent substitution on the $(\text{Ti},\text{Zr})^{4+}$ sublattice, but that the substitution occurs with either decreased lead vacancy or increased oxygen vacancy charge compensation. The data obtained supports this conclusion and indicate clearly that oxygen vacancies are formed to neutralize the charge. This is illustrated in Fig. 7.

In this case the initial weight gain is believed to occur in the manner described for nobia.

* Abstracted from R. L. Holman, Intrinsic and Extrinsic Nonstoichiometry in the lead Zirconate-Titanate System (Ph.D. thesis), LBL-880, July 1972.

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4. PROCESSING PARAMETERS AND THE PROPERTIES OF LITHIUM FERRITE

Gautam Bandyopadhyay and Richard M. Fulrath

Lithium ferrite (LiFe_2O_4) possesses some unique properties, necessary for use in computer memory cores. Its processing involves problems due to the loss of lithium and oxygen during the sintering step. The purpose of this investigation is to correlate the sintering parameters, stoichiometry, and the effect of dopants, to the densification, microstructural characteristics, hysteresis loop parameters, and dc resistivity of lithium ferrite. This information will not only help to control the properties of lithium ferrite, but also would be helpful to understand the "ferrites" as a whole.

a. Weight Loss and Chemical Changes

Composition of the starting material is always an important factor in the processing of electronic ceramics. The influence of composition on the weight loss of lithium ferrite has been determined by thermogravimetric analysis in air. The results tend to indicate an increasing oxygen loss with the increase of Fe_2O_3 content in the composition. This type of material loss is found to be enough to cause significant deviation from the stoichiometry and in some cases led to decomposition with the appearance of second phases. All the principal phases that may

exist in this ferrite system (e.g., LiFe_5O_8 , LiFeO_2 , Fe_3O_4) have their important X-ray peaks almost at the same angles. But the use of I_{311}/I_{400} ratio (both planes are for the spinel phases) qualitatively indicated the relative amounts of spinel phase and LiFeO_2 phase present. Figure 1 shows a sharp change in the surface composition of the sintered ferrites on the stoichiometric line. Predominantly spinel phase was observed on the Fe_2O_3 -rich side of the composition, and LiFeO_2 phase on the lithia-rich side.

The study of the surface composition was also done by using stoichiometric specimens and sintering time, temperature, and packing powder compositions as the variables. The two-step decomposition of lithium ferrite as originally postulated by Salmon et al.¹ under somewhat different conditions seems to explain the results adequately. Furthermore it seems that Fe_2O_3 , if present, always tends to go into solid solution with the spinel ferrite as Fe_3O_4 and as FeO in the LiFeO_2 phase.

In all the sintered ferrites a significant difference has been observed between the bulk and the surface composition. This has been attributed to the different amount of material loss from the two regions.

Fig. 1. X-ray data for specimens sintered at 1150°C for 2 hours in 1 atm O_2 , using "stoichiometric" packing powder. (XBL 731-2050)

Fig. 2. Dependence of coercive force (H_c) and dc resistivity on the composition. All the specimens were sintered at 1150°C for 2 hours in 1 atm. O_2 , using "stoichiometric" packing powder. (XBL 731-2048)

b. Processing Parameters and the Properties

Most of the sintering runs were done at 1150°C for 2 hours in 1 atm O_2 and using stoichiometric packing powder. Some isothermal sintering runs were made for various lengths of time. In some cases packing powder compositions were varied. Sinter densities of Fe_2O_3 -rich specimens were found to be lower than those of lithia-rich specimens sintered under identical conditions. This is believed to be due to increased anion vacancy concentration in the lithia-rich compositions.

Extensive exaggerated grain growth has been observed in the lithia-rich specimens sintered at 1150°C for 2 hours. On the other hand, very small grains with pores exclusively on the grain corners have been

Fig. 3. Grain size and bulk resistivity data from some isothermal sintering runs. "Stoichiometric" packing powder and 1 atm O_2 were used in all the sintering runs. (XBL 731-2047)

observed in the Fe_2O_3 -rich specimens. This is in accordance with the results reported in the literature² for some other ferrites.

The variation of coercive force (H_C) and dc resistivity with the composition is shown in Fig. 2. H_C has been calculated from the B-H hysteresis loop. Resistivity was measured by using a guard ring method which allowed the measurement of the surface and bulk resistivity separately. Lower H_C value on the lithia-rich side is probably due to larger grains. Variation of resistivity may be due to the presence of higher Fe^{+2} concentration in the Fe_2O_3 excess compositions due to greater oxygen loss. Lower surface resistivity than that of the bulk for an individual specimen is expected because of greater oxygen loss from the surface resulting in higher Fe^{+2} concentration.

Experimental runs on the isothermal

sintering have indicated that grain size can also have significant effect on the resistivity value. In Fig. 3, average size of the largest grains and dc resistivity have been plotted against sintering time. It is clear that discontinuous grain growth is always accompanied by an increase in resistivity. This is possible if grain boundaries act as the easy conducting path. Oxygen loss is expected to occur preferentially from or along the grain boundaries. This would result in a higher Fe^{+2} concentration in the boundaries than that in the bulk and therefore a lower resistivity along the grain boundary.

Studies on the effect of packing powder compositions on the sinterability and properties of lithium ferrite are being done. There are indications that significant control on the final properties can be achieved by this method. The effect of selective additives like NiO , $NiFe_2O_4$, MnO_2 , etc. are also being studied with an aim to achieve better control of the magnetic properties.

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5. DIFFUSION OF GASES IN GLASS

Joseph Masaryk and Richard M. Fulrath

The use of ceramics as either pressure or vacuum envelopes at high temperatures requires knowledge of the ability of gases to penetrate these materials. From a practical standpoint fused silica glass is of interest because it exhibits the highest overall permeability to gases of any ceramic material. Consequently, gaseous diffusion in fused silica is being studied in an effort to define the precise diffusion mechanisms and the effects of thermal history and impurities on this process.

By far the largest impurity in standard commercial silicas is water in the form of hydroxyls (OH), which may be present in the range from 10 to 1000 ppm, depending on method of manufacture. These hydroxyls reduce the density of the glass at room temperature. Another factor that affects the density is the thermal treatment of the glass which affects the density by increasing it with increasing stabilization temperature.

Very thin (0.07 mm) fused silica diffusion

membranes were subjected to a series of treatments designed to independently vary the water content and stabilization temperature. After each treatment the He diffusivity was measured as a function of temperature in the range -78 to 165°C. The activation energies for diffusion of He in fused silica as a function of treatment are:

$\Delta H(\text{diffusion}), \text{ cal}$	Sample Treatment	Density, g/cc
4900±50.0	1000°C, vacuum	2.202
5114±27.5	1000°C, 1 atm H ₂ O	2.201
4967±27.0	1200°C, vacuum	2.204
5140±50.0	1200°C, 1 atm H ₂ O	2.203

These results indicate that water content and stabilization temperature, which affect other properties significantly, do not appreciably affect the diffusion properties of He in fused silica. The small increase in activation energy with increasing stabilization temperature is probably due to the increasing density, which decreases the size of the interstice through which the He atom must move. Even though OH content decreases the density, the activation energy for diffusion is increased, because the extra oxygen added to the structure provides a steric hindrance to the movement of He.

An interesting observation was noted on the diffusion of He through these thin-walled membranes. Diffusivity data obtained on these membranes over the past two years has consistently exhibited activation energies about 20% lower than those reported in the literature, which used membranes about 1 mm thick. Consequently, the diffusion of He through a 1 mm membrane was measured in order to distinguish any instrumentation effects. This thicker membrane exhibited activation energies comparable to those reported in the literature. Work is currently under way to determine if surface, compositional, or thermal differences between the membranes exist.

A model describing the diffusivity of nonatomic gases in fused silica yields the expression

$$D = \frac{Kd^2}{6h} \underbrace{\left(\frac{e^{\frac{h\nu}{2KT}} - e^{-\frac{h\nu}{2KT}}}{e^{\frac{h\nu^*}{2KT}} - e^{-\frac{h\nu^*}{2KT}}} \right)^2}_{D_0} e^{-\frac{\Delta H_0}{RT}} \quad (1)$$

This model, which considers the motion of the gas atom as it moves between equilibrium solubility sites, yields three independent variables: the distance the atom moves between these sites, d ; the vibration frequency

Fig. 1. Comparison of experimental diffusivity data for helium in fused silica with a plot of Eq. (1), using the parameters of $d = 2.5 \text{ \AA}$, $\nu = 6.9 \times 10^{12} \text{ sec}^{-1}$, $\nu^* = 7.8 \times 10^{12} \text{ sec}^{-1}$ and $\Delta H = 6100 \text{ cal/mole}$. (XBL 726-6371A)

Fig. 2. Variance of the value of the pre-exponential factor, D_0 , with temperature of the Arrhenius equation for helium diffusion in fused silica. (XBL 726-6372A)

quency on the atom in the constriction between two sites, ν^* ; and the activation energy for this process, H . Due to the amorphous nature of fused silica it is impossible to accurately calculate the values of these variables. Thus a least squares analysis was performed on the best fit of the model to diffusivity data of He in SiO₂, which appears in the literature (Fig. 1). This analysis yields values of 2.5 Å for d , $7.8 \times 10^{12} \text{ sec}^{-1}$ for ν^* , and 6100 cal/mol for the ΔH . These values compare favorably with

Fig. 3. Comparison of experimental permeability data for helium in fused silica with a plot of Eq. (2), using the parameters of $d = 2.5 \text{ \AA}$, $v^* = 7.8 \times 10^{12} \text{ sec}^{-1}$ and $\Delta H_k = 4600$. (XBL 726-6375A)

those reported in the literature for the vibration frequency in a solubility site and the activation energy calculated using the standard Arrhenius equation.

For the diffusion of non-reactive gases in glass, there has been some question as to the temperature dependence of the pre-exponential factor, D_0 , in the Arrhenius expression. Several authors have argued that the expression $D = D_0 \exp(-\Delta H/RT)$ better describes this process. No theoretical justification related to this process has been put forth to justify the insertion of a factor of T . Using the model derived in this work, it can be seen that D_0 can be expressed in terms of fundamental parameters of the material and diffusing species. If one then substitutes the determined values of d and v^* in this expression, D_0 can be calculated as a function of temperature (Fig. 2). This yields an essentially temperature-independent value of D_0 from 300°K for He in fused silica.

At moderate gas pressures the solution of a monatomic gas in glass obeys Henry's law. This yields the relationship that the Permeability = Diffusivity $\times$ Solubility. If we combine the diffusivity model of the present work with the solubility model of the investigation previous to this one, we obtain the permeability expression

$$K = \frac{1}{6} \frac{d^2}{h} \left(\frac{h^2}{2\pi m k T} \right)^{3/2} \frac{N_5}{\left(e^{\frac{h\nu}{2kT}} - e^{-\frac{h\nu}{2kT}} \right)^2} 2e^{-\Delta H_1/RT} \quad (2)$$

Use of values of the independent variables determined from the diffusivity and solubility models yields reasonable agreement of the permeability model with data in the literature on He permeation in fused silica (Fig. 3). The permeability model need not be confined strictly to gases in glass, but can be applied to any gas which does not dissociate or react and diffuses interstitially in any solid.

6. RESEARCH PLANS FOR CALENDAR YEAR 1973

Richard M. Fulrath

Processing studies in both lead zirconate titanate and lithium ferrite have established the important process parameters that influence the achievement of high density ceramics. During 1973 the major effort will be directed to establishing how intrinsic and extrinsic defect structures affect the electronic and magnetic properties of polycrystalline ceramics with controlled density and grain size.

The studies on grain boundary structures in ceramics will concentrate on high density aluminum oxide. Samples of suitable geometry for grain boundary permeation and diffusion studies were fabricated in 1972. The first measurements will be to determine the grain boundary permeation of He in high density controlled grain size alumina.

Sintering studies by high temperature scanning electron microscopy will continue on submicron Al_2O_3 . Studies on UO_2 and systems containing a liquid phase will be initiated during 1973.

The mechanical properties of glass-ceramics will be studied because recent work in this group has indicated that the glass matrix composition can influence the fracture. Fracture initiation will be measured to determine if a microplastic zone is exhibited by glass.

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Richard M. Fulrath and Associates

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A. THEORETICAL SOLID STATE PHYSICS

Marvin L. Cohen, Principal Investigator

Introduction. New insights were gained into the properties of the amorphous state by investigating successively more complex crystalline polytypes of Ge and Si.

Superconducting transition temperatures were related to lattice mode softening, and limits on the maximum superconducting transition temperature were explored.

1. SEMICONDUCTORS AND INSULATORS

Marvin L. Cohen

A variety of semiconductors and insulators were investigated theoretically, using the Empirical Pseudopotential Method (EPM). Layer compounds (SnS_2 and SnSe_2), narrow gap semiconductors (lead salts and CdTe-HgTe alloys), and complex polytypes of Ge and Si were analyzed, in addition to the more popular materials like the III-V and II-VI semiconductors. The potentials used in these calculations were obtained through experimental data input. Optical, X-ray Photoelectron Spectroscopy (XPS), and Ultraviolet Photoelectron Spectroscopy (UPS) were investigated and used to fit energy levels. Calculations of the density of states energy band structures, dielectric functions as a function of frequency and wave vector, and electronic charge density plots were made possible by using the EPM scheme. The results allowed interpretation of the experimental data and new insights into the electronic structure of semiconductors and insulators.

For the case of Ge and Si polytypes, investigations were made of the electronic structure of four modifications of these crystals: FC-2 (face-centered cubic with two atoms per cell), 2H-4 (hexagonal with four atoms per cell), BC-8 (body-centered cubic with eight atoms per cell), and ST-12 (simple tetragonal with 12 atoms per cell). It was possible to use the same atomic pseudopotential for Ge or Si in each of the modifications and to account for the crystal structure change via the structure factor. In this way long-range order was preserved, but short-range order was continually changed. It was found that some of the experimental properties of the amorphous state were simulated through the changes in the structure factor. In particular it was found that the presence of fivefold rings (present only in ST-12) was important if some of the amorphous properties

were to be simulated. These studies yielded information about the origin of the optical structure in addition to suggesting schemes for systematic studies of the amorphous state.

XPS and UPS have gained renewed popularity in the last few years and it is expected that there will be enormous growth in this area in the next few years. Detailed theories are not available as yet, but it appears fairly certain at this time that the measured spectra reflect the valence band density of states. Our theoretical calculations support this conclusion. In fact, systematic studies going from covalent to more ionic crystals (Ge, GaAs, ZnSe) show ionic energy gaps which appear in the experimental spectra and in the theoretical calculations. In addition, amorphous films appear to have spectra similar to density of states calculations for the ST-12 systems. It was also possible to show some fundamental relations between gaps in the spectra, energy band splittings, and ionicity parameters.

Charge density calculations were done for PbTe, HgTe, CdTe, $\text{Cd}_{1-x}\text{Hg}_x\text{Te}$ alloys, cubic and hexagonal ZnS, and for model semiconductors to study the relation between bonding and electronic or crystal structure. For the $\text{Cd}_{1-x}\text{Hg}_x\text{Te}$ case it was possible to explore the charge distribution of the top valence band and bottom conduction band as a function of alloying. This is particularly interesting in this case since the alloy becomes a zero gap semiconductor near the HgTe end. Model pseudopotentials were used in charge density calculations and these showed the role of the potential in determining the bonding. For the cubic and hexagonal ZnS case the dependence of bonding on structure was explored and it was shown that for an ideal c/a ratio a dipole moment exists. It was speculated that changing the c/a ratio might reduce the polarization, leading to a method for determining c/a ratios. A new scheme was developed for charge density calculations, allowing calculations based only on a few k -points in the Brillouin zone. This scheme considerably reduces the computer time involved in the calculation.

For the first time, dielectric functions as a function of wave vector and frequency were calculated. The materials studied were Si, Ge, GaAs and ZnSe. These functions can be used for electron energy loss studies, bonding studies, and other theoretical investigations of semiconductors.

2. METALS

Marvin L. Cohen

The electronic band structure and charge densities were studied for some metallic systems. For the case of aluminum, detailed charge density plots showed the electronic distribution in the unit cell. Fourier transforms of the charge density were used to calculate the X-ray scattering factors, and the results were shown to be in good agreement with experiment. Non-local pseudopotentials which were successful in determining the electronic structure of noble metals and transition metals were extended to transition metal compounds. In particular, NbN was studied in detail. The band structure and charge density calculation should prove useful in studying materials like NbN, which is a high temperature superconductor.

3. SUPERCONDUCTIVITY

Marvin L. Cohen

Limitations on the maximum superconducting transition temperature were studied. In particular the dielectric formulation was used to show that Umklapp processes were necessary if very high transition temperatures were to be attained.

The role of phonon softening in superconductivity was also investigated. New sum rules and expressions for the electron-phonon interaction parameter were derived. Using these expressions, the observed transition temperatures are related to phonon softening in some materials, and predictions are made about materials not yet found to be superconducting.

4. RESEARCH PLANS FOR CALENDAR YEAR 1973

Marvin L. Cohen

We have begun studies of NbC and plan to use charge density plots to attempt to understand the superconducting properties of this crystal and similar crystals.

Calculations of NaCl in the zincblende and rocksalt structure have been started, and the role of charge distributions in determining crystal structure will be explored.

The II-IV-V₂ chalcopyrite crystals will be studied with emphasis on ZnGeP₂. These crystals are interesting since they resemble

the III-V semiconductors, and the differences between them and the III-V semiconductors give information about the underlying electronic structure of these types of materials. They are also good nonlinear materials.

We also hope to explore the relationship between bonding and valence band gaps, do further studies on Ge and Si polytypes, photoelectron studies, and further charge density studies.

5. 1972 PUBLICATIONS AND REPORTS

Marvin L. Cohen and Associates

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* Not supported by IMRD funds.

B. FAR INFRARED PROPERTIES OF SOLIDS

Paul L. Richards, Principal Investigator

1. RESONANCE MODES IN ANTIFERROMAGNETIC (Co,Mn)F₂ AND (Fe,Mn)F₂

Paul L. Richards and William E. Tennant

The insulating antiferromagnetic iron group fluorides are perhaps the best characterized magnetic system. Recent neutron diffraction experiments have attempted to study mode localization in alloys of these materials. Far infrared measurements, which are restricted to wave vector $q \approx 0$, are much more sensitive than neutron diffraction and thus provide complementary information.

In Fig. 1 we show the frequency and line widths of magnetic resonance modes which appear in our far infrared powder spectra of the alloy system (Co,Mn)F₂. These modes are identified as antiferromagnetic resonances in pure MnF₂ (at 9 cm⁻¹) and in pure CoF₂ (at 36 cm⁻¹), and isolated defect modes at 115 cm⁻¹ in nearly pure MnF₂ and 27 cm⁻¹ in nearly pure CoF₂. We also see modes due to clusters of two (32 cm⁻¹) and three (35.5 cm⁻¹) defects in CoF₂ and due to neighbors of isolated defects (67-75 cm⁻¹) in CoF₂.

The alloy system (Fe,Mn)F₂ shows very

similar behavior to the data shown for the (Co,Mn)F₂ system, except that cluster defect modes are not observed.

Simple Ising model calculations of the mode frequencies agree quite well with the data, as shown in Table I. More detailed calculations recently obtained from Oxford are being compared with the results.

Fig. 1. Center frequencies and line widths of resonant modes observed by far infrared Fourier spectroscopy on powder specimens of alloys of CoF₂ and MnF₂. (XBL 7210-7118)

Table I. Frequencies of impurity modes.

Mode	Ising Frequency Given By	Host			
		CoF ₂		FeF ₂	
		Ising	Experiment	Ising	Experiment
Mn Defect in Host	$\omega_D = H_{AD}' - 2S_H I'(1) + 8S_H I'(2)^\dagger$	33 cm ⁻¹ *	28.5 cm ⁻¹	49 cm ⁻¹	50 cm ⁻¹
Neighbors of Mn Defect	$\omega_N = H_{AH} - 2S_H I_H(1) + 7S_H I_H(2) + S_D I'(2)^\dagger$	79	67, 71(2) 72, 75	79	78-80
Pairs of Mn Defects	$\omega_P = H_{AD}' - 2S_H I'(1) + 7S_H I'(2) + S_D I_D(2)$	31.2**	32	53	not observed
Triplets of Mn Defects	$\omega_T = H_{AD}' - 2S_H I'(1) + 6S_H I'(2) + 2S_D I_D(2)$	34.8**	35.5	57	not observed

[†] Formula and values of $I(1)$, $I(2)$, H_A , and S taken from R. A. Cowley and W. J. L. Buyers, Rev. Mod. Phys. **44**, 406 (1972).

*

** Uses experimental value for $S_H I'(2)$ computed from defect mode frequency.

These experiments answer a long-standing question: as early as 1962 extra far infrared modes were seen in normally pure FeF_2 and CoF_2 . We now know them to be due to Mn^{2+} as a substitutional impurity.

1. Samples obtained from Dr. E. Catalano, Lawrence Livermore Laboratory.

2. BALLOON-BORNE FAR INFRARED SPECTROMETER

John C. Mather, Paul L. Richards and David P. Woody

A far infrared spectrometer has been developed that can be flown with a high altitude balloon for use in astrophysical studies. The principal features of the system are a liquid-helium cooled polarizing interferometer and a germanium bolometer. The spectrometer is calibrated for absolute radiometry with an anticipated accuracy of better than 0.1°K for a Rayleigh-Jeans source.

This spectrometer is being interfaced to a balloon gondola developed by Professor Kinsey Anderson of the Berkeley Space Sciences Laboratory. The system is designed to make high resolution measurements of the cosmic background radiation in the $6\text{--}20\text{ cm}^{-1}$ spectral region. Low resolution measurements in this spectral region made from rockets and balloons have yielded contradictory results.

Three crucial improvements in the system were made during the year. First, the antenna pattern is now defined by a long polished copper reflecting cone at the entrance to the spectrometer. This cone has no stray reflections as lenses do. Without this cone, radiation received from the earth and the background would have been stronger than the signal of interest. Second, the detector has been improved by an order of magnitude by replacing the InSb detector used formerly with a very small Ge bolometer fed by immersion optics. This was necessary because of the very small signal entering the spectrometer (only $2.5 \times 10^{-11}\text{ W}$ over the entire bandwidth of the 2.7° background radiation). Third, the cryogenic efficiency has been improved in several ways, allowing sufficient time to take data in flight before the liquid helium boils away. A superfluid pump was developed to circulate the liquid on command. Gas flow systems were devised

to cool the optics with gas instead of liquid. And finally, a process for coating metal with polyethylene was developed to reduce the power emitted by those objects in the beam that are allowed to remain warm.

A first flight is anticipated early in 1973.

3. IDEAL PERFORMANCE FROM POINT CONTACT JOSEPHSON JUNCTIONS¹

Paul L. Richards and Yuan Taur

Point contact superconducting Josephson tunnel junctions have long been considered attractive devices for high frequency mixers and detectors. They are highly nonlinear, show response beyond $\sim 10^{12}\text{ Hz}$, and have low noise. Extensive device calculations based on the resistively shunted junction (RSJ) model have recently shown that Josephson effect microwave mixers can exhibit conversion gain. This is in contrast to classical resistive diode mixers in which the ratio of signal power to intermediate frequency power (conversion efficiency) must be less than or equal to unity.

The RSJ model assumes that the current through an actual Josephson junction is the sum of a Josephson current $I = I_0 \sin(2e/h) \times \int V(t)dt$ and a quasiparticle current $I = GV$. In order to test the applicability of the RSJ model to Nb point contact junctions, we have measured the dc current-voltage characteristics of such junctions with and without applied rf radiation and compared them with calculations² from the model. Noise in the measuring circuit has a strong influence on such curves. When noise is added to the theoretical model, near perfect agreement with experiment is obtained, as is shown in Fig. 1. These results show that calculations of device performance from the RSJ model can be expected to be reliable, and that high performance mixers should be possible.

1. A portion of this research was supported by the U.S. Office of Naval Research and the U.S. Army Research Office, Durham.
2. Computer calculations by F. Aurracher, Department of Electrical Engineering, U.C., Berkeley.

Fig. 1(a) Experimental and theoretical I-V curves for a Nb point contact with $T = 4.2^\circ\text{K}$ and normalized frequency $\Omega = 0.16$ at 36 GHz. The data are shown as a heavy solid line. The thin solid line is the prediction of the RSJ model without noise and the thin dashed line is the prediction of the RSJ model with 100K thermal noise.

(b) Experimental and theoretical dependence of the zeroth and first step heights on rf current. The theory is fitted to the data at the two marked calibration points. This two-point calibration is used to fit all curves in Fig. 2(a)-(b). The resistance value deduced is the same as that required to fit the static I-V curve in the low voltage region. (XBL 728-3744)

4. INSTRUMENTATION FOR FOURIER TRANSFORM SPECTROSCOPY

Richard L. Aurbach and Paul L. Richards

Development of instrumentation for Fourier transform spectroscopy proceeded along two lines: construction and testing of a new Fourier transform spectrometer and computer programming for real-time data analysis.

Last year construction was begun on a

polarizing interferometer. This instrument takes advantage of the the superior properties of the free-standing wire grid polarizer as a beam-splitting element as compared to the thin Mylar dielectric beam splitter; normally used in Michelson interferometers in the far infrared. The efficiency of dielectric beam splitters is strongly frequency-dependent due to interference effects, and has a peak value of only 60%. The free standing wire grid polarizing beam splitters, on the other hand, have a constant efficiency of nearly 100% up to a cutoff frequency which is determined by the wire spacing. Construction of the polarizing interferometer has now been completed and it is in general laboratory use over the frequency range from 1 to 80 cm^{-1} .

The output of a Fourier transform spectrometer is an interference pattern (or interferogram) which is the Fourier transform of the desired spectrum. Hence, the basic tool of data analysis is the Fourier transform. In order to provide a quasi-real-time data analysis capability, our data collection system is interfaced with a PDP 11/20 minicomputer. Data acquisition is computer controlled. The data can be stored in active memory and/or Fourier transformed. Using a fast Fourier transform algorithm developed at the Argonne National Laboratory, 1000 data points can be transformed in about 3 seconds.

Other mathematical operations include apodization (correction for the finite length of the data), coding of repeated data runs (for improvement of the signal-to-noise ratio), convolutional phase correction (correction for sampling errors), division of one spectrum by another (to remove the spectral profile of the spectrometer from the spectrum), and calculation of the logarithm of the spectrum (for computation of the absorption coefficient). Either the data or the transformed spectrum can be stored in active memory, displayed on an oscilloscope, plotted on an x-y recorder, punched on paper tape for permanent storage, listed on the teletype, or punched on cards for analysis on a general purpose computer.

5. FAR INFRARED STUDIES OF γ -IRRADIATED RUBY

Richard L. Aurbach and Paul L. Richards

The formation of color centers in irradiated ruby has been studied by numerous researchers for over ten years. This work has been stimulated by the importance of ruby as a laser material, particularly since

ultraviolet radiation from laser flash lamps has sufficient energy to form these centers.

One model which has been proposed to explain these color center effects involves charge transfer reactions which lead to the formation of Cr^{2+} and Cr^{4+} ions in the crystal. EPR experiments predict that the Cr^{4+} ion in ruby should absorb radiation in the 7 cm^{-1} region. Thermal conductivity measurements suggest that Cr^{2+} may absorb radiation near 6 and 65 cm^{-1} .

We have measured the far infrared transmission of an 18-cm long ruby rod¹ over the frequency range from 3 to 400 cm^{-1} . The rod has been measured after γ -irradiation from a ^{60}Co source, after bleaching with white light, and after annealing at high temperature. The γ -irradiated sample shows broad background absorption due to damage-induced phonon transitions and also weak absorption lines at 6.4, 7.5, and 59 cm^{-1} . Work is in progress to positively identify these lines.

A second sample¹ which contains 100 ppm Ba is also been studied. It is too short (1.9 cm) to show the weak lines found in the first sample, but does show the broad background effects as well as a strong radiation induced impurity mode at 150 cm^{-1} .

1. Obtained from R. L. Forman, NBS, Washington, D.C.

6. GENERATION OF TUNABLE FAR INFRARED RADIATION BY MIXING TWO DYE LASERS

Kei-hsiung Yang, James Morris, Paul L. Richards, and Y. Ron Shen

In order to make far infrared difference frequency generation into a practical spectroscopic tool, we have developed the dual-beam one-cavity dye laser source, shown in Fig. 1. When a Glan-Thomson prism is inserted into the cavity of a dye laser, the horizontal and vertical polarizations are sent in separate directions. Diffraction gratings can then be used as frequency selective reflectors to return the beams back to the dye cell. By turning the gratings independently, the laser can oscillate simultaneously with orthogonal polarizations at two different frequencies. For a ruby pumped dye laser operating on I₂C iodide in dimethyl sulfoxide, the two lasers can be varied over the bandwidth from 810 to 8400 Å . The laser output can be mixed in nonlinear crystals to generate tunable far infrared radiation over the frequency range from 5 to beyond 190 cm^{-1} . Many nonlinear crystals such

Fig. 1. Schematic diagram of the dual-beam one-cavity dye laser used for generation of the tunable far infrared radiation. The symbol $\odot$ indicates that the optical polarization is perpendicular to the plane of the diagram, $\uparrow$ indicates that the polarization is parallel to the plane of the diagram. The nonlinear mixing crystal is mounted on a rotatable disk. The difference frequency signal at $\omega_1 - \omega_2$ is normalized by the sum frequency signal at $\omega_1 + \omega_2$. (XBL 731-5600)

as LiNbO_3 , ZnO , CdS , CdSe , and ZnS have been investigated for this purpose. For generating far infrared radiation at frequencies below 50 cm^{-1} , LiNbO_3 is the best material tried. For frequencies higher than 50 cm^{-1} , ZnO (which can be collinearly phase-matched as high as 190 cm^{-1}) is more suitable. This dual-beam one-cavity dye laser scheme has also been tested successfully with rhodamine 6G dye and a flash lamp pump. The flash-lamp-pumped laser can be pulsed repetitively, thus greatly increasing the usefulness of the method.

7. NONLINEAR OPTICAL SPECTROSCOPY OF $\chi^{(2)}$ IN LiNbO_3

James Morris, Kei-hsiung Yang,
Paul L. Richards, and Y. Ron Shen

The dual-beam one-cavity dye laser scheme described above has been used to investigate the dispersion of the nonlinear susceptibility $\chi^{(2)}(-\omega_1-\omega_2)$, $(\omega_1, -\omega_2)$ in LiNbO_3 . The far infrared difference frequency power at $\omega_1-\omega_2$ is measured as a function of the dye laser frequency ω_2 , with the laser frequency ω_1 kept constant. The absorption coefficient at $\omega_1-\omega_2$ must be known in order to relate the measured power to $\chi^{(2)}$. Absorption coefficients as large as 1500 cm^{-1} (which can not be measured by linear spectroscopy) are obtained by varying the crystal orientations and measuring the width of the phase matching curve. In order to normalize laser beam fluctuations, the signal at the sum frequency, $\omega_1+\omega_2$, was generated by the reflection method from the surface of GaAs. The expected enhancement of $\chi^{(2)}$ due to polariton effects has been observed when the difference frequency $\omega_1-\omega_2$ is close to a transverse optical phonon mode in LiNbO_3 . We also plan to measure the dispersion of $\chi^{(2)}$ in CdS .

8. RESEARCH PLANS FOR CALENDAR YEAR 1973

Paul L. Richards

With the exception of the Josephson junction work which is now being supported by the Office of Naval Research and the interferometer construction, which is now completed, all of the projects discussed will be continued. Exploration of the zero field far infrared resonance modes in the iron group fluorides will continue on the $(\text{Fe},\text{Co})\text{F}_2$ and $(\text{Zn},\text{Mn})\text{F}_2$ systems, and Zeeman splittings of the modes already discovered in the $(\text{Fe},\text{Mn})\text{F}_2$ and $(\text{Co},\text{Mn})\text{F}_2$ systems will

be measured. A search will be made for effects related to localization of the modes observed. It is anticipated that construction will be completed in early 1973 on the balloon-borne radiometer for cosmic background measurements. At least one balloon flight should be carried out during FY 1974. Studies of the far infrared electron spin resonance of samples of Al_2O_3 containing Cr^{2+} and Cr^{4+} will be carried out in order to interpret data on radiation damaged ruby. Development of the dye laser difference frequency source will be continued and further studies of the nonlinear coefficients of optical materials in the phonon frequency range will be carried out. It is anticipated that a program to explore the far infrared properties of liquid crystals will be initiated.

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‡ Partially sponsored by the ONR (Office of Naval Research).

C. SUPERCONDUCTIVITY

Gene I. Rochlin, Principal Investigator

1. SHUNTED JOSEPHSON JUNCTIONS: EXPERIMENTS AND MODEL

Paul K. Hansma and Gene I. Rochlin

Our previous work on externally shunted Josephson junctions has been extended to junctions constructed in a non-inductive configuration as shown in Fig. 1. By simplifying the sample geometry in this way possible complications due to the inductance of the open loop shunts previously used have been eliminated, and a very precise fit to the McCumber shunted junction model can be made. In order to further explore the nature of the model an exact mechanical analog, a driven, damped pendulum, was constructed and its characteristics examined. By plotting the mechanical analogs of the junction I-V characteristics, the time-averaged rotation rate vs. applied torque for the pendulum system, the McCumber solutions can be examined in a detailed way to gain physical insight into the behavior of weak-link devices.

Fig. 1. A non-inductive externally shunted Josephson junction. The outer two junctions are shunted by Sn-Ag tunnel junctions, since the Ag is deposited first. The center junction is left unshunted to monitor junction quality. (XBL 721-2208)

2. BEHAVIOR OF WEAK-LINK DEVICES NEAR THE JUNCTION-LIKE TO BULK-LIKE TRANSITION

Yeong-du Song and Gene I. Rochlin

The dc characteristics of small thin-film tin microbridges both with and without applied rf field has been studied at temperatures below the superconducting transition temperature of tin. When the temperature and impurity-dependent coherence length, ξ is greater than the bridge length, L , the temperature dependence of the dc supercurrent agrees with predicted behavior of ideal Josephson tunnel junctions. In this regime, the rf-induced ac steps on the junction characteristics occur only at harmonics of the rf frequency, e.g., at voltages $V = nh\omega/ze$, and the power dependence of the steps is in good agreement with Josephson ac effect theory. When the temperature is decreased or the coherence length otherwise shortened so that $\xi < L$, the rf sensitivity is markedly decreased and vast numbers of small steps appear at subharmonic and fractional harmonic voltages $mV = nh\omega/ze$. This clearly shows that an ac Josephson effect is observable only for Josephson analog systems when the coherence length is less than or comparable to the weak link of the system, and supports recent arguments that the ac Josephson effect in liquid helium has, in fact, never been observed, as $L \gg \xi$ for the geometries used in these experiments.

The frequency and temperature dependence of the Dayem effect (enhancement of the zero-voltage step with applied microwave power) has led us to a new theory of this effect based on increased quasiparticle lifetimes very near the transition. Our data very clearly show that the usual explanation of phase-fluctuation stabilization by the rf field is untenable for our samples.

3. INDIUM-BARRIER-INDIUM TUNNELING JUNCTIONS

Michael D. Jack and Gene I. Rochlin

We have successfully produced high-quality In-In and In-Pb superconducting tunnel junctions by a completely new junction fabrication technique--glow discharge dissociation of a liquid fluorocarbon. By this method we have been able to controllably vary the junction resistance over 12 orders of magnitude, and to produce the first In-In tunnel junctions ever reported. The second derivative of the In-In characteristic, as

Fig. 1. Second-derivative trace of our In-I-In tunnel junctions as a function of voltage, compared with the earlier published Al-I-In work of McMillan, Powell, and Dynes.

(XBL 728-6763)

shown in Fig. 1, enables us to resolve fine structure in the In phonon density of states not observable in the Al-In junctions previously used. In addition, low resistance junctions produced by this technique show excellent Josephson characteristics, and all the other structures associated with truly high-quality tunnel junctions. These are the first "synthetically" (i.e., by means other than thermal oxidation) prepared tunnel junctions yet produced which behave according to the ideal Josephson model and are free of shorts and other irreproducibility-creating physical structures.

4. CHARACTERIZATION OF TUNNELING BARRIERS

Duncan E. McBride and Gene I. Rochlin

We have obtained excellent agreement between the experimentally measured current-voltage characteristics of metal-insulator-metal tunnel junctions and a model calculation based on a trapezoidal barrier. By comparing the junction characteristic, over many orders of magnitude of current, with the results of the calculation, we are able to determine not only $\phi^{3/2}$, but the oxide layer thickness s and the barrier height ϕ . The height is then related to the optical band gap of the insulator (Al, Cr, and V oxides) while the thickness is compared with that determined by capacitance measurements. Discrepancies in the thickness as determined by the two types of measurement are being analyzed in terms of a random distribution of high and low spots in the oxide layer.

5. OBSERVABILITY OF QUASIPARTICLE-PAIR INTERFERENCE CURRENT IN SUPERCONDUCTING WEAK LINKS

Franz Auracher, Paul L. Richards, and Gene I. Rochlin

The effect of the phase-dependent pair-quasiparticle interference conductance, $G_1 \cos \phi$, on the behavior of Josephson weak links has been theoretically calculated. For the case of G_1/G_0 constant and equal to -0.95 , where G_0 is the ordinary tunnel conductance, the Josephson phase-time relationship was numerically integrated to yield the current-voltage characteristics. As shown in Fig. 1, large deviations are predicted for the static I-V characteristic in the presence of such an interference current, the most marked effect being the presence of a time-average reverse supercurrent, indicated by the current-voltage characteristic falling below the normal tunneling asymptotic line. The effects of this term on the rf-induced steps, although observable in principle, are small enough to be neglected on device applications.

A preliminary search for this effect in Sn-I-Sn thin-film tunnel junctions near T_c has indicated that the interference term is not observed. However, it was necessary to reduce the Josephson current by temperature or magnetic field in order to make the McCumber parameter, β_c , small enough to look

Fig. 1. Normalized static I_0 - V_0 curves for various values of the junction capacitance parameter $\beta_c = ze_1 C / h G_0$ and the pair-quasiparticle interference parameter $\gamma = J_1 / J_0$.

(XBL 7211-7182)

for the effect, and the negative evidence is thus inconclusive, since the ratio of the interference to the normal conductance may depend on the magnitude of the Josephson dc current.

6. RESEARCH PLANS FOR CALENDAR YEAR 1973

Gene I. Rochlin

The projects listed above will be completed, and the search for the pair-quasiparticle interference term will be continued.

7. 1972 PUBLICATIONS AND REPORTS

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John Clarke, Principal Investigator

1. NON-EQUILIBRIUM EFFECTS IN SUPERCONDUCTORS

John Clarke

We have observed a new effect in superconductors which are in non-equilibrium. The experimental configuration is as follows. A strip of aluminum is evaporated onto a glass microscope slide and oxidized, and a strip of tin evaporated across the aluminum to form a tunnel junction. The junction is then masked off with varnish, except for a small window in the middle of the junction. A strip of copper is evaporated diagonally across the window, to form a probe. Any voltage generated across the probe and the tin strip can be measured with a superconducting voltmeter (SIUC).

With the tin in the superconducting state, a current I is passed between the aluminum and tin strips, injecting quasiparticles into the tin side of the junction and removing pairs from it. The tin is therefore in a non-equilibrium situation, with an excess population of quasiparticles and a depleted population of pairs. Furthermore, there is an imbalance in the quasiparticle populations above and below the Fermi surface of the tin. Under these circumstances, there is a difference between the chemical potential of the pairs, measured by the tin strip, and the quasiparticle voltage, measured by the copper strip. It can be shown theoretically that for higher injection voltages (well above the gap Δ of the tin) the voltage difference is

$$V = \frac{I\tau_Q}{2e^2 N(0) g_{NS}}$$

where τ_Q is the relaxation time for the quasiparticle imbalance, Ω the volume of the tin overlaying the aluminum, $N(0)$ the density of states in the tin, and g_{NS} the low voltage tunneling conductance between the tin and the copper. Figure 1 shows the quantity

$$\zeta = V g_{NS} I^{-1}$$

plotted against temperature. The experimental points are a good fit to a curve proportional to Δ^{-1} , from which we deduce

$$\tau_Q = 4 \times 10^{-10} \Delta(0)/\Delta(T)$$

This result is in good agreement with the theoretical estimate.

This experiment is the first to demonstrate the existence of such non-equilibrium potential differences in superconductors. There are several physical situations in which these effects are important: an example is given in section 5.

Fig. 1. Plot of $\zeta = V g_{NS} I^{-1}$ against temperature, averaged over all samples. (XBL 731-2042)

2. ELECTRON FOCUSING IN BISMUTH: A NEW METHOD OF MEASURING THE CALIPER OF A FERMION SURFACE

John Clarke and Louis Schwartzkopf

We have observed electron focusing in bismuth in the presence of magnetic fields of

Fig. 1. Comb structure: A--plan view, showing interlocking combs; B--side view, showing electron orbits. (XBL 7112-4954)

Fig. 2. Resistance between combs evaporated on the trigonal face of a bismuth crystal as a function of magnetic field. Maxima are visible at $H_0/2$ and $H_0/4$, and minima at H_0 and $H_0/3$. (XBL 731-5625)

a few gauss. Two interlocking superconducting combs are evaporated onto the surface of the crystal, (Fig. 1A) and the resistance between the two combs $R(H)$ measured at liquid helium temperature as a function of a magnetic field parallel to the teeth. $R(H)$ has a minimum when the electrons are focused between teeth

of the two different combs, and a maximum when they are focused between teeth of the same comb. From the spacing of the teeth and the values of H at which the extrema occur, the caliper of the Fermi surface in a plane perpendicular to the sample surface can be determined.

Single-crystal samples were grown from $99.999 + \%$ bismuth, and spark-cut to the proper orientation. The spark-cut surface was chemically polished, and cleaned in a glow discharge. The tin combs were then evaporated onto the cleaned surface without exposing the sample to the atmosphere. The resistance between the combs was measured by a Josephson junction device (SLUG) in an automatic self-balancing circuit.

Figure 1B shows our results from a sample in which the plane of the combs is perpendicular to the trigonal axis. The observed positions of the major maximum and minimum in $R(H)$ agrees very well with the value H_0 calculated from the known Fermi surface parameters (see Fig. 2). In fact, we believe that our method may provide the most accurate way of directly measuring the caliper of a Fermi surface. The extrema in $R(H)$ at $H_0/2$, $H_0/3$, etc., correspond to electron focusing between more distant teeth of the combs.

We plan to complete the work on bismuth by obtaining data in the other two crystallographic orientations. We expect to see the hole orbits in these cases. We hope to be able to see similar focusing effects between just two superconducting strips. In addition, we plan to study other materials, such as copper, with this technique.

3. AN IMPROVED DC SQUID

John Clarke and James B. Kruger

For a number of years we have used double Josephson junction devices (dc SQUIDS) to measure tiny magnetic fields and voltages. During the past year we have made two improvements which have greatly enhanced both the sensitivity and the ease of operation of our devices.

The first improvement is to couple the ac SQUID into a resonant circuit, as indicated in Fig. 1. The SQUID is biased at a non-zero voltage by means of a dc current I_0 , and a small dc magnetic field is applied at the resonant frequency of the tank circuit, ν . If the dc magnetic flux is $n\phi_0/2$, where ϕ_0 is the flux quantum, the signal developed

Fig. 1. DC SQUID connected in resonant circuit. (XBL 731-5620)

across the tank circuit is at a frequency 2ν , and is almost entirely rejected by the tank circuit. If the dc flux is $(n + 1/2)\phi_0/2$, the signal is at a frequency ν , and is amplified by the Q of the tank circuit, typically 100. This signal is detected with a lock-in detector, and the output fed back into a coil coupled to the SQUID to provide negative feedback. The device is therefore the null sensor in the feedback system: this procedure overcomes almost all sources of $1/f$ noise.

The voltage developed across the tank circuit when the dc flux is changed from $n\phi_0$ to $(n + 1/2)\phi_0$ is given by

$$\Delta V_T = \frac{\omega L_T \phi_0}{L},$$

where $\omega/2\pi$ is the resonant frequency of the tank circuit, and L and L_T are the inductances of the SQUID and tank circuit. For $\omega/2\pi = 10^5$ Hz, $L = 10^{-9}$ H, and $L_T = 2$ mH, we find $\Delta V \approx 2.5$ mV. This signal is two orders of magnitude greater than that achieved from rf SQUIDS or dc SQUIDS directly coupled to room temperature amplifiers. The ultimate resolution of a dc SQUID is thought to be on the order of $10^{-6} \phi_0/\text{Hz}$: it is hoped that the large signal now available from the tank circuit, about 5 mV/ ϕ_0 , will enable us to approach this resolution.

The second improvement is the development of a toroidal SQUID. In this configuration, the device is completely self-screening against fluctuations in the external magnetic field. It has proved simple and reliable to

use, and we feel that this configuration will prove to be the most sensitive of the SQUIDS.

4. A JOSEPHSON JUNCTION BOLOMETER

John Clarke and Gary I. Hoffer

Last year we reported on the use of the superconductor-normal metal-superconductor Josephson junction as a highly sensitive infrared bolometer element. At that time we had demonstrated the feasibility of such a device. In the past year we have concentrated on improving the reliability and optimizing the sensitivity of the bolometer system. We can now make junctions reproducibly on (low heat capacity) sapphire substrates, and junctions stored and recycled over periods of up to eight months have shown no change in electrical properties. The chief limitation on the sensitivity of the bolometer has been noise in the SLUG that we have used to measure the voltage across the junction. We have recently acquired an rf SQUID which, when used in our bolometer system, provides a voltage sensitivity 100 times better than that of the SLUG.

We have investigated the use of thin bismuth films as an infrared absorbing coating for our bolometers. The infrared transmission in the frequency range 0 to 50 cm^{-1} was measured, and it appears that a relative absorption close to the theoretical maximum of $3/4$ can be obtained with ~ 300 Å bismuth films on sapphire. We plan to test the far infrared sensitivity of the device in the near future.

5. RESISTANCE OF SNS SANDWICHES AT VERY LOW TEMPERATURES

John Clarke, Stuart M. Freake, James B. Kruger, and Michael L. Rappaport

We have verified our phenomenological theory which allows us to determine the superconducting transition temperature, T_c , of "normal" metals whose T_c is below that which present technology can attain. The theory predicts that the resistance, R , of a superconducting-normal metal-superconducting (SNS) sandwich should decrease with decreasing T and that the shape of the R vs. T curve determines the BCS interaction parameter, $N(0)V$, in N and thus $T_c \approx 1.14 \phi_0 \times \exp[-1/N(0)V]$.

Of course, T_c for N should be independent

Fig. 1. Resistance normalized to bulk value versus reduced temperature T/T_c , where T_c is the critical temperature for tin.

(XBL 731-5622)

of S. This has indeed been shown to be the case by making sandwiches which are identical in all respects except for the S. In particular, using a known superconductor (Ir) as N, both Pb and Sn (S) gave the accepted value for Ir of $N(0)V = 0.11$.

Specimens were then made of Pb-Rh-Pb, Pb-Ag-Pb, Pb-Cu-Pb, and Pb-Mg-Pb. The first three types were run in our dilution refrigerator from 18 mK to 7K. A careful analysis of the data indicated that at the lowest temperatures it is necessary to include the effect of the self-field of the measuring current on the resistance. Efforts at calculating this effect have provided improved fits to the data and have suggested alternative measuring schemes.

The Pb-Mg-Pb specimens indicated a dirty SN interface due to the reactivity of the Mg. To eliminate this problem, a new sputter-etch system was designed and built and will soon be in operation.

In addition, the resistance of the Sn-Ir-Sn specimens near the T_c of Sn was analyzed as a non-equilibrium problem of quasiparticle injection into a superconductor (see section 1). According to the Clarke-Tinkham theory, the quasiparticles should travel dissipatively into S a distance proportional

to $[\Delta(T)]^{-1/2}$, where $\Delta(T)$ is the energy gap in S at the temperature T. A computer fit of the data to the theory (see Fig. 1) then determined the branch-crossing relaxation time $\tau_Q = 1.3 \times 10^{-10}$ sec, in excellent agreement with the theory.

6. A SEARCH FOR SUPERCONDUCTIVITY IN DEGENERATE SEMICONDUCTORS

John Clarke, Richard Dalven, Stuart M. Freake, James B. Kruger, and Michael L. Rappaport

The change of susceptibility of a semiconductor was used to detect the superconducting transition down to 18 mK. Since only three semiconducting superconductors are known (GeTe, SnTe, SrTiO_3), the discovery of additional ones should provide new insight into the relationship between the normal state properties (band structure, carrier concentration) and the mechanisms (electron-phonon, electron-exciton) for superconductivity.

The samples tested were AuTe_2 , GaP, SnSe, GaSe, α -Sn, HgSe, PbSe, and Ge. From the magnetization curves of α -Sn and HgSe, it appeared that part of these specimens went

superconducting. However, since both β -Sn and Hg are by themselves superconductors, inhomogeneous samples could account for the results.

The single crystal of high purity natural (isotope concentration) Cd included in each run to be sure the apparatus was working had $T_c = 0.520 \pm 0.001$ K, in agreement with recently published values, but differing considerably from Roberts' values (0.54-0.56 K).

* Handbook of Chemistry and Physics, 48th edition, edited by R. C. Weast, 1967.

7. 1/f NOISE IN THIN FILMS

John Clarke and Richard F. Voss

A study was undertaken to determine the physical mechanism of 1/f noise through an investigation of the simplest and best understood system purported to exhibit 1/f noise, that of thin metal films. Although most investigators have observed 1/f noise in metal films only when the metal was non-uniformly deposited in the form of small "islands," one group has reported the noise in continuous gold forms and suggests that metal films and other systems produce 1/f noise according to:

$$\left(\frac{\Delta V}{V}\right)^2 \approx \frac{2 \times 10^{-3}}{N} \frac{\Delta f}{f}$$

where N = total number of charge carriers in the sample. For pure metals one then requires cross-sectional areas of order 10^{-8} cm² or smaller to observe the 1/f noise above amplifier background noise.

A technique was developed for cutting the samples from thin films evaporated onto glass slides, using a diamond knife and a two-dimensional micromanipulator. The technique proved extremely versatile, allowing the construction of samples in various geometries with multiple lead connections and dimensions ranging from a few microns to several centimeters.

The initial measurements on gold films were limited by electrical pickup from the current source and only those strips with non-uniform cuts containing "necked down" regions produced observable noise. Since this was not the simple reproducible system desired, an attempt was made to use bismuth

films where the lower carrier concentration ($10^{17}/\text{cm}^3$ as opposed to $10^{22}/\text{cm}^3$) would allow larger dimensions and greater noise. With bismuth the 1/f noise was often easily observable but usually only when the samples carried currents close to their burnout value. Samples exhibiting noise showed definite visible deterioration after an hour or so of use. Recent experiments with an improved configuration to eliminate noise due to pickup and the current supply showed that the 1/f noise power in bismuth was at least three orders of magnitude below that predicted by the formula above, provided the sample was operated at currents well below the burnout level. Also, with the improved configuration, 1/f noise of the predicted magnitude was not observed in gold films.

In conjunction with the experiments, a theoretical study of possible 1/f noise theories was begun. All present theories are inadequate. Non-equilibrium statistical mechanics and nonlinear theories seem to be the most promising. A computer simulation of Brownian motion with a cubic restoring force gives a 1/f spectrum over at least several decades of frequency. However, experimentally there seems to be little correlation between nonlinearity in the current-voltage characteristic and the measured 1/f noise.

The theoretical work will be continued. An attempt will be made to set a more quantitative upper limit to the 1/f noise in metal samples, and to correlate the onset of observable noise with irreversible changes in the system.

8. QUANTUM TRANSITIONS IN A DC SQUID

John Clarke and James L. Paterson

We have observed quantum transitions in dc SQUIDS at currents below the critical current I_c for the case of an asymmetric current feed in zero applied field (Fig. 1A). The Sn-Sn oxide-Sn junctions are shunted by silver disks. A tin ground plane (not shown), insulated from the SQUID by 500 Å of SiO₂, was used to decrease the loop inductance.

Consider the case in which the junctions are identical with currents of Φ_0/L each, where L is the loop inductance. We assume that the SQUID quantizes flux exactly in the limit $m \gg 1$. The current I divides inversely as the inductances of the current paths (Fig. 1B). For $L \gg L_J$, the junction inductance, essentially all of I flows through junction A. When I_A reaches Φ_0/L ,

Fig. 1. (a) SQUID consisting of two Sn-SnO_x-Sn tunnel junctions with Ag shunts. A 500 Å layer of SiO and a Sn ground plane are evaporated over the structure.

(b) Schematic representations of SQUID with maximum asymmetry in the current feed. (XBL 731-5621)

junction A admits n flux quanta to the loop and momentarily produces a voltage V , where

$$\int_0^t V(t)dt = n\phi_0$$

Consider the case where n is always unity. The flux quantum in the loop is produced by a circulating current ϕ_0/L which reduces the current through A by ϕ_0/L . The current I can now increase by ϕ_0/L before another flux quantum enters the loop and another voltage pulse is produced. This process continues until $I_B = m\phi_0/L$ and the loop contains $m\phi_0$. These voltage pulses for $I < I_C$ have not been reported previously.

Fig. 2. Current (vertical, 500 μ A/cm) versus voltage (horizontal, 50 μ V/cm) for asymmetric SQUID. $T = 1.3$ K. (XBB 7212-6310)

For a SQUID with hysteresis in the I-V characteristic there is the possibility that these voltage pulses will trigger a transition from the superconducting to the finite voltage state. Figure 2 shows the I-V trace swept at ~ 100 Hz for a SQUID at 1.3 K with $I_C \approx 1.3$ mA. For $I \geq 0.7$ mA there exists a stable state at finite voltage. Several transitions are seen, separated in current by 101 ± 10 μ A. The transitions for positive I appear to carry approximately equal weight (there can be only one transition per current sweep). The measured value of ϕ_0/L for the SQUID was 107 ± 5 μ A, in good agreement with the observed spacing.

The analysis which we have performed for two junctions in parallel has applicability to the general case of many junctions in parallel. This system has been proposed for use in high speed computer memories.

9. RESEARCH PLANS FOR CALENDAR YEAR 1973

John Clarke

The measurement of pair-quasiparticle potential differences will be continued. We aim to obtain data when the quasiparticles are injected into the superconductor near the gap edge: from these results we should obtain the variation of the relaxation time, τ_Q , as a function of energy. These results

can then be applied to related effects in non-equilibrium superconductors.

The new technique for determining the caliper of Fermi surfaces will be applied to bismuth in different orientations, and perhaps also to copper. From the results we expect to be able to make accurate estimates of the various calipers. We hope to be able to calculate the amplitude of the oscillations theoretically.

The toroidal SQUID and the resonant detection technique will be further developed, and incorporated in a feedback system. The ultimate noise limitations of this system will be determined. We hope to make this system our basic laboratory measuring instrument, as a more sensitive replacement for our present devices.

The resolution of the Josephson junction far infrared bolometer will be measured. If the sensitivity meets our expectations, the bolometer will be developed into a hardened device for a number of applications. We expect to collaborate with Professor Richards in these applications.

More data will be obtained on the resistance of SNS junctions at low temperatures. From these data we hope to be able to make quantitative estimates of the transition temperatures of a number of materials, for example, Cu, Ag, Mg, and Rh.

More degenerate semiconductors will be tested to see if they become superconducting at low temperatures. The transition temperatures of any materials which are superconducting can then be correlated with theoretical estimates. The scope of the measurements is dependent on the availability of suitable samples.

The measurements of $1/f$ noise in thin films of bismuth and gold will be completed. We hope to be able to correlate the noise with the structure of the films as determined by electron microscopy. We also plan to perform further computer calculations on our nonlinear model.

A project will be initiated to construct a thin film gradiometer, using a dc SQUID and our resonant circuit readout technique. It is hoped that this device will be very stable, and reliable enough to be used in a non-laboratory environment.

We plan to start measurements on the resistance of very clean Pb-Cu-Pb sandwiches. We hope to see abrupt changes in resistance as a function of temperature, arising from

the discrete energy levels of quasiparticles "trapped" in the normal layer.

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* R. Dalven, presently with the Dept. of Physics, U. C. Berkeley and a participant with IMRD.

D. EXPERIMENTAL SOLID STATE PHYSICS AND QUANTUM ELECTRONICS

Y. Ron Shen, Principal Investigator

1. RESONANCE RAMAN SCATTERING IN InSb

Peter Y. Yu and Y. Ron Shen

Resonance Raman scattering in InSb near the E_1 transition has been measured at low temperatures for various different configurations with a tunable dye laser. The experimental curves show a resonance peak at an incident photon energy appreciably higher than the energy of the E_1 peak in the reflectivity spectra, contrary to the predictions of existing theories. Double resonance in the Raman tensor involving transitions in the band continuum is proposed to explain the result.

the similarity of their molecular structure. A few Raman modes, particularly the intermolecular ones, exhibit quasidiscontinuous changes at the phase transitions. These changes are qualitatively interpreted as the result of modification of the intermolecular interaction induced by the phase transitions.

We have investigated the Raman spectra of some smectic compounds in the spectral region of 5 to 2000 cm^{-1} . Emphasis was given to the temperature dependence of the low frequency modes near the phase transitions. We observed a low frequency mode in the solid phase of the related compounds diethylazoxybenzoate (DEAB) and diethylazoxycinnamate (DEAC). This mode shifts abruptly to lower frequency and decreases in intensity at the transition to smectic while vanishing in the isotropic phase. Since the frequency of this mode is found to be independent of the length of the end groups, we interpret it as arising from the intermolecular dipole-dipole interaction between the carboxyl groups. The shift in the frequency of this mode is attributed to increase in the spacing of the layered structure of the smectic phase. This is consistent with the results obtained from X-ray. The same interpretation explains the decrease in intensity of this mode. No low frequency modes were observed in other smectic compounds such as the higher homologues of azoxybenzene, presumably because of the difference in the intermolecular interaction.

2. RESONANCE RAMAN SCATTERING AND LUMINESCENCE IN Cu_2O

Peter Y. Yu, Yves P. Petroff, and Y. Ron Shen

Luminescence spectra of Cu_2O at various temperatures excited by a tunable dye laser showed no evidence of the existence of excitonic molecules (or biexcitons) as suggested recently by Gross et al. A pair of previously unreported peaks with an exceptionally strong temperature dependence has been observed below 3°K.

We also obtained strong resonance enhancement in the 220 cm^{-1} Raman line of Cu_2O at the Γ_{12} -phonon-assisted threshold of the forbidden 1s yellow exciton. A consistent theoretical interpretation is found. It shows that the line is due to scattering of two Γ_{12} phonons and the resonance enhancement is strongly affected by the exciton lifetime. The latter effect has never been considered or observed before in resonance Raman scattering.

4. RAYLEIGH-WING SCATTERING NEAR THE NEMATIC-ISOTROPIC TRANSITION

Nabil M. Amer, David Y. S. Lin, and Y. Ron Shen

While fluctuations in the direction of molecular alignment can give rise to light scattering in a liquid crystal, fluctuations in the orientation of individual molecules can also cause light scattering. The latter is usually described as Rayleigh-wing scattering. We have investigated for the first time the Rayleigh-wing scattering in a nematic compound MBBA in both the nematic and the isotropic phases as a function of temperature. Our results indicate that the spectrum of the Rayleigh wing can be decomposed into two Lorentzians, a narrow one and a broad one. As the temperature approaches the isotropic-nematic transition from the isotropic side, both Lorentzians become narrower, indicating a slowing down in the orientational fluctua-

3. RAMAN AND RAYLEIGH SCATTERING IN LIQUID CRYSTALS

Nabil M. Amer, David Y. S. Lin, and Y. Ron Shen

We have investigated the Raman spectra of four nematic members of the homologous series 4, 4'-bis (alkoxy) azoxybenzene in the solid, nematic, and liquid phases for a spectral range of 10 to 1900 cm^{-1} . These spectra show great similarity, as one would expect from

tions. The phenomenon is somewhat similar to that of spin fluctuations in a magnetic system near the order-disorder transition.

5. WAVELENGTH-MODULATION SPECTROSCOPY OF SOLIDS

Yves P. Petroff, Stanley E. Kohn, Jeffrey A. Stokes and Y. Ron Shen

We have used our wavelength-modulation spectrometer to study optical properties of semiconductors and metals. The high sensitivity and high resolution of the spectrometer enables us to find many new features in the solid spectra. The spectrometer has also been used to study the changes in the spectra induced by external perturbations. Our results on InP, GaP, ZnGeP₂, SbSI, Ag, Cu, and Au have been obtained and compared with the spectra calculated by Marvin L. Cohen and his associates using the empirical pseudopotential method. The agreement between theory and experiment is very good.

6. DISPERSION OF NONLINEAR OPTICAL SUSCEPTIBILITIES

Arnold Schmidt, Don Bethune, and Y. Ron Shen

The dispersion of the nonlinear susceptibility $\chi^{(2)}$ close and above the band gap of semiconductors is of considerable interest.

A setup to measure nonlinear susceptibilities against a known reference (e.g., Quartz) was developed. The fundamental frequency is provided by a dye laser pumped by ruby light or its second harmonic, or alternatively by a flash lamp pumped dye laser. The spectral region covered extends from 4100-9000 Å. The detection system employs gated electronic integrators. The first investigations will be on III-V compounds above their band gap. Measurements on InAs have been started.

Another experiment planned is the measurement of the nonlinear susceptibility of alkali halides. Since these materials have a center of symmetry, the nonlinear susceptibility is very small. However, at the exciton frequency a large resonance enhancement is to be expected.

7. SECOND-HARMONIC GENERATION FROM A SOLID-STATE PLASMA

Arnold Schmidt, Eric G. Hanson, and Y. Ron Shen

Plasmons in metals have been excited by a number of different processes. One conceivable process is the generation of a plasmon by a two-photon excitation. A plasmon decaying radiatively will emit photons of twice the frequency, which might be detected. Silver is a suitable candidate for such an experiment since its plasmon frequency (~3300 Å) is in reach of available tunable dye lasers. Attempts have been made to obtain a sufficiently powerful laser at 6600 Å.

Cresyl violet has been investigated, either pumped with frequency-doubled light from a Nd laser or by a flash lamp. Both methods have led to lasers which might be powerful enough for the planned experiment.

8. FAR INFRARED GENERATION BY OPTICAL MIXING

James R. Morris, Patrick K. H. Yang, Paul L. Richards, and Y. Ron Shen

We have built a novel dye laser cavity which allows two orthogonally polarized, separately tunable laser beams to be generated simultaneously in one cavity. Since both beams are generated in a common pumped region and utilize the same output mirror, the problem of aligning the beams for some dual beam nonlinear optical spectroscopy experiments including far infrared generation by optical mixing is greatly simplified. We have used this system in preliminary investigations of LiNbO₃, ZnO, ZnS, CdS, and CdSe as possible far infrared sources in the region 10 to 250 cm⁻¹. LiNbO₃ seems to be the best candidate for the low frequency range, say below 50 cm⁻¹ because of its high electro-optic coefficient. ZnO seems to be the best candidate around 180 cm⁻¹ due to its lower absorption coefficient. CdS may be useful in the frequency range below 180 cm⁻¹ also. We are also using the nonlinear mixing process to directly measure the absorption coefficient of LiNbO₃ in a region inaccessible to ordinary far infrared techniques and to measure the dispersion of the lowest order nonlinear susceptibility.

9. COHERENT PHONON GENERATION BY OPTICAL MIXING

Patrick K. H. Yang, Paul L. Richards, and Y. Ron Shen

We have examined the feasibility of generating high frequency coherent phonons in a superlattice by optical means. With the help of the lattice momentum, phase-matched optical generation of coherent phonons with frequencies higher than 50 GHz appears feasible. We have considered two cases theoretically: 1) direct conversion of millimeter or submillimeter photons in a piezoelectric superlattice, and 2) optical mixing of two laser beams in a non-piezoelectric superlattice.

10. SPECTRAL BROADENING IN THE SELF-FOCUSED LIGHT

George K. L. Wong and Y. Ron Shen

It has been shown recently that, at least for nanosecond pulse excitation, moving foci are responsible for the observation of small-scale filaments in Kerr liquids. Most observed characteristics of the filaments can be explained by the moving-focus model. In particular, spectral broadening of light from a filament can be interpreted as due to phase modulation acquired by the self-focused light in traversing the nonlinear medium. However, no controlled systematic experiment on spectral broadening has yet been performed to check the validity of the interpretation. Such an experiment is important in view of the fact that spectral broadening has long been used as evidence to support the self-trapping model. We have performed the first experiment on spectral broadening with nanosecond input pulses under controlled input conditions. We show that there exists, in fact, semiquantitative agreement between theory and experiment. Induced partial trapping or nonlinear diffraction of light in a filament can occur, but its effect is only on the detailed structure of the broadened spectrum.

11. RESEARCH PLANS FOR CALENDAR YEAR 1973

Y. Ron Shen

We shall continue our research on resonance Raman scattering and luminescence in several different crystals. We shall also continue our work on wavelength-modulation spectroscopy and hope to extend the operating range of

the spectrometer further into the vacuum UV. We shall conduct measurements on the dispersion of nonlinear optical susceptibilities in many nonlinear media. We also plan to spend more effort in studying the linear and nonlinear optical properties of solids.

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8. Y. Petroff, P. Y. Yu and Y. R. Shen, Luminescence in Cu₂O--Exciton Molecules or Not, Phys. Rev. Letters 29, 1558 (1972) (LBL-1133).
9. J. Koo, Y. R. Shen, and R. R. L. Zucca, Effects of Uniaxial Stress on the E_1^0 -Peak of Silicon, Sol. State Commun. 9, 2229 (1971). (Not listed last year) (LBL-146).

Papers presented

1. S. Kohn, Y. Petroff, P. Y. Yu and Y. R. Shen, Wavelength Modulation Spectra of PbS, PbSe, PbTe, and SnSe, Conference on the Physics of IV-VI Compounds and Alloys, Philadelphia, Pa., March 1972 (LBL-456).
2. George K. L. Wong and Y. R. Shen, Study of Spectral Broadening of Light in a Filament Induced by a Moving Focus, Seventh International Quantum Electronics Conference, Toronto, Canada, May 1972 (LBL-468 Abstract).
3. Nabil M. Amer, Y. S. Lin, and Y. R. Shen, Raman Study of Some Smectic Liquid Crystals Near Phase Transitions, Fourth International Liquid Crystal Conference, Kent State University, Kent, Ohio, August 1972 (LBL-836 Abstract).
4. Nabil M. Amer, Y. S. Lin, and Y. S. Shen, Rayleigh-Wing Scattering Near the Nematic-Isotropic Transition, Fourth International Liquid Crystal Conference, Kent State University, Kent, Ohio, August 1972 (LBL-835 Abstract).
5. Y. R. Shen, Optical Wavelength-Modulation Spectroscopy, Invited talk presented at the First International Conference on Modulation Spectroscopy, Tucson, Arizona, November 1972 (LBL-1402).
6. S. Kohn, Y. Petroff, and Y. R. Shen, Wavelength Modulation Spectra of GaSe, GaS, and Alloys, First International Conference on Modulation Spectroscopy, Tucson, Arizona, November 1972 (LBL-1407).
7. Y. Petroff, S. Kohn, and Y. R. Shen, Optical Spectra of CsI, CsBr, ZnGeP₂, and SbSI, First International Conference on Modulation Spectroscopy, Tucson, Arizona, November 1972 (LBL-1409).
8. Y. Petroff, S. Kohn, and Y. R. Shen, Effect of Carrier Concentration on the Reflectivity Spectrum of Ge and InSb, First International Conference on Modulation Spectroscopy, Tucson, Arizona, November 1972 (LBL-1410).

LBL reports

1. S. Kohn, Y. Petroff, Y. R. Shen, and P. Yu, Wavelength Modulation Spectra of PbS, PbSe, PbTe, and SnSe, LBL-456, April 1972.
2. K. H. Yang, P. L. Richards, and Y. R. Shen, Coherent Phonon Generation by Optical Mixing in a One-Dimensional Superlattice, LBL-889, June 1972.
3. S. E. Kohn, P. Y. Yu, Y. Petroff, Y. R. Shen, Y. Tsang, and M. L. Cohen, Electronic Band Structure and Optical Properties of PbTe, PbSe, and PbS, LBL-1132, August 1972.
4. Nabil M. Amer and Y. R. Shen, Low Frequency Raman Mode in Smectic Liquid Crystals Near the Phase Transitions, LBL-1156, September 1972.
5. Ricardo Zucca and Y. R. Shen, A Wide Range Wavelength Modulation Spectrometer, LBL-1184, October 1972.
6. P. Y. Yu, Y. R. Shen, Y. Petroff, and L. M. Falicov, Resonance Raman Scattering at the Forbidden Yellow Exciton in Cu₂O, LBL-1192, October 1972.
7. Y. R. Shen, Optical Wavelength-Modulation Spectroscopy, LBL-1402, November 1972.
8. S. Kohn, Y. Petroff, and Y. R. Shen, Wavelength-Modulation Spectra of GaSe, GaS, and Alloys, LBL-1407, November 1972.
9. Y. Petroff, S. Kohn, and Y. R. Shen, Optical Spectra of CsI, CsBr, ZnGeP₂, and SbSI, LBL-1409, November, 1972.
10. Y. Petroff, S. Kohn, and Y. R. Shen, Effect of Carrier Concentration on the Reflectivity Spectrum of Ge and InSb, LBL-1410, November 1972.

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DEGREES AWARDED IN 1972

Ph.D. Degrees

1. Charles J. Bruggemann, The Effect of One-Dimensional Plastic Strain Waves in α -Phase Titanium-Aluminum Alloys (LBL-802, April).
2. Shih-Ger Chang, High Temperature Spectroscopy and Thermodynamics of Titanium Oxide and Vanadium Oxide (LBL-450, March).
3. Mervyn Ming-Hwa Chiang, Reactive and Inelastic Scatterings of Molecular Ions (LBL-474, February).
4. Mary McIvor Conway, The Low-Temperature Heat Capacity of Cerium Metal (LBL-827, May).
5. Roy Tom Coyle, Vaporization Kinetics of Magnesium Nitride (LBL-136, January).
6. David Hoover Feather, Mass Spectrometric Studies of Inorganic Vapors (LBL-844, September).
7. Paul Kenneth Hansma, Externally Shunted Josephson Junctions (LBL-498, March).
8. Alan Butler Harker, Reaction Kinetics of the Photolysis of NO_2 , and the Spectra and Reaction Kinetics of the Free Radicals in the Photolysis of the $\text{Cl}_2\text{-O}_2\text{-CO}$ System (LBL-1114, September).
9. Robert Louis Holman, Intrinsic and Extrinsic Non-Stoichiometry in the Lead Zirconate-Titanate System (LBL-880, August).
10. Jacob Jorñé, Electrochemical Behavior of the Alkali Metals in Propylene Carbonate (LBL-1111, September).
11. Dale Henry Klain, Dislocation Modeling of Strain-Rate Phenomena (LBL-800, March).
12. Kaoru Kojima, A Study of the Mechanism of Electropolishing of Copper (LBL-140, February).
13. Shen-Maw Lin, Molecular Beam Kinetics (LBL-891, September).
14. Ronald John Livak, Spinodal Decomposition and Coarsening in Cu-Ni-Fe Alloys (LBL-1107, September).
15. Marshall Harvey Mendelsohn, Reactions of Heptasulfur Imide and the Heptasulfur Imide Anion (LBL-495, March).
16. Farghalli Abdel Rahman Mohamed, High Temperature Creep in Metals at Intermediate and Low Stresses (LBL-1183, November).
17. Robert Allan Olstad, Mass Spectrometric Investigation of Laser-Induced Vaporization of Binary Solid Compounds (LBL-1177, December).
18. Kenneth Alan Strom, Reactions of Hydrogen in Liquid Ammonia Systems (LBL-1408, November).
19. Teh Yu Tan, Behaviors of Inelastic Electrons (LBL-432, January).
20. Francis Ting-yuan Wang, A Kinetic Study of the Stepwise Hydrolyses of the Hydroborate and the Octahydrotriborate (LBL-411, February).

D.Eng. Degrees

1. Mathur Ramachandran Veera Raghavan, Structure and Mechanical Properties of Fe-Ni-Co Alloys with and without Carbon (LBL-477, March).

M.S. Degrees

1. Rajani Bhushan Agnihotri, Chemical Transport Reaction Analysis for Crystal Growth of Binary and Ternary Chalcogenides (LBL-1404, December).
2. Kwame Ankra, Unidirectional Solidification of Al-CuAl₂ Eutectic (LBL-1182, December).
3. Ara Joseph Baghdasarian, Corrosion Resistance of TRIP Steels (LBL-806, May).
4. Peter Paul Bihuniak, The Mechanism of Zinc Oxide Single Crystal Vaporization (LBL-867, June).
5. Richard Wyant Headrick, Design Criteria for Solid Electrolyte Electrochemical Cells (LBL-839, July).

6. Kanithi Hemachalam, Evaluation of Optimal Process Parameters for the Production of Superconducting Niobium-Tin in Relation to Pilot Plant Design (LBL-1108, June).
7. Wade Alan Horwood, Factors Controlling the Fracture Toughness of Cryogenic Alloys (LBL-1121, December).
8. John Arthur McMahon, Structure, Strength and Toughness of Fe/Cr/C Martensitic Steels (LBL-1181, December).
9. Pirooz Mohazzabi, The Kinetics of Vaporization of Barium Sulfate (LBL-1416, December).
10. Mark Walter Perra, Nuclear Magnetic Resonance Study of GP Zone Formation in Al-4%Cu (LBL-838, June).
11. Saleem Anwar Shaikh, Chemical Vapor Deposition of GaAs_{1-x}P_x Reactor Design and Growth Kinetics (LBL-1149, September).
12. Craig Barlow Shumaker, Initial Stage Sintering of Copper and Nickel (LBL-1110, August).
13. Chi-Shine Cliff Tao, Polycrystalline Spinel from Powders Prepared by Freeze Drying Technique (LBL-876, June).
14. Nader Vahdat, The Corrosion of Iron Rotating Disks (LBL-873, June).
15. Sarwan Kumar Wason, Screening of Candidate Materials for Bio-Compatibility (LBL-None, March).
16. Boon Wong, Permeation of Silicate Liquids into Sintered Magnesia Compacts (LBL-877, September).

1972 RESEARCH SEMINARS

<u>Date</u>	<u>Title</u>	<u>Speaker</u>
2/17	The Stress-Induced Martensitic Transformation of Fe-Ni-Cr Austenitic Stainless Steel Single Crystals	Glen A. Stone (GS)*
2/17	Intrinsic Non-Stoichiometry in the Lead Titanate-Lead Zirconate System	Robert L. Holman (GS)*
3/9	Kinetics of Vaporization of Zinc Oxide	Professor W. Hirschwald Free University of Berlin Germany
3/9	Effect of Martensitic Substructure on Mechanical Properties	Mathur Raghavan (GS)*
3/9	Ordered Arrays of Steps on High Index Faces of Platinum Crystals	Bernard Lang (PD)†
3/9	The Resistance of TRIP Steels to Hydrogen Embrittlement (H.E.)	Robert A. McCoy (PD)†
3/21	Low Temperature Magnetic Studies of Metal-Ammonia Compounds	N. J. Sienko Cornell University Department of Chemistry New York
3/23	Antiphase Domains in Terrestrial and Lunar Anorthite	Wolfgang Müller (PD)†
3/23	A Study of the Mechanism of Electropolishing of Copper	Kaoru Kojima (GS)*
3/23	Current Gain in Josephson Junctions	James L. Paterson (GS)*
4/6	On the Stability of Dislocation Loops Near Free Surfaces	Jagdish Narayan (PD)†
4/6	Correlation of Thermo-Mechanically Varied Microstructures with Superconducting Properties of Nb ₃ Sn Processed by a New Powder Metallurgy Technique	B. Naga Babu (GS)*
4/6	Low Temperature Heat Capacity of Cerium Metal	Mary I. Conway (GS)*
4/20	Anodic Behavior of Titanium Carbide in Sulfuric Acid	Dr. H. E. Hintermann Swiss Watch Research Laboratory Neuchatel, Switzerland
5/31	Surfaces, Relaxation, Reconstruction, Adsorption	Leonard Dobrzynski Department of Physics University of California Irvine
7/6	Dislocation Motion Through a Random Array of Point Obstacles	Dale Klahn (GS)*
7/6	Electrochemical Behavior of the Alkali Metals in Propylene Carbonate	Jacob Jorñé (GS)*
7/10	Structural Chemistry of Polynuclear Transition Metal Cyanides	A. Ludi Universität Bern Switzerland

<u>Date</u>	<u>Title</u>	<u>Speaker</u>
8/25	Behavior of Type II Superconductors with A(XV) and B(I) Structure in High Magnetic Fields	Professor E. Saur Director of the Institute of the Angewandte Physik University of Giessen Germany
10/19	Spinodal Decomposition in Cu-Mn-Al Alloys	Marcel Bouchard (PD) [†]
10/19	The Oscillator Strength of Ti-O α System and VO Green System	Shih-Ger Chang (GS)*
10/19	A Systematic Approach to the Band Structure of III-V Semiconductors	Jeffrey Stokes (GS)*
11/30	Mass Spectrometric Investigation of Laser-Induced Vaporization of Binary Solid Compounds	Robert Olstad (GS)*
11/30	A Method for Increasing the Fracture Toughness of Ultra-High Strength Steels	William Wood (GS)*
11/30	Surface Features in the Evaporation of As Single Crystals	Dr. G. Rosenblatt (C)** Penn State
12/7	Use of Ceramics as Surgical Implants	Ralph Leonard Clemson University South Carolina

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