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MATERIALS AND CHEMICAL
SCIENCES DIVISION

**Annual Report 1989
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MASTER

Materials
Sciences

Chemical
Sciences

Fossil
Energy

Energy
Storage
Systems

Health and
Environmental Sciences

Exploratory Research
and Development
Funds

Work for
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REMARKS BY THE DIVISION DIRECTOR

The 1989 calendar year saw a number of events of significance for MCS D.

The Advanced Materials Laboratory (AML) was formally dedicated on June 23, 1989. The speakers at the ceremony were Dr. Robert O. Hunter, Jr., Director, Office of Energy Research, DOE, and LBL Director David A. Shirley. The building was already partially occupied at that time, and within a few months a substantial fraction of the space was occupied and research in a number of areas was under way. However, the full use of the building has been delayed by the necessity of accommodating to changes in general standards for the safe handling of toxic and flammable materials, as well as to changes in the relevant building codes. The building codes have been changed twice since the conceptual design for the AML was completed, and extensive modifications are required before all the research now planned for the AML can be conducted consistently with current standards. It has been decided to install a central monitoring and warning system that will also control the ventilation system in response to various kinds of spills and accidents. In the meantime, research is constrained to the use of reduced quantities of certain substances, and the initiation of some research is being delayed.

Construction of the Advanced Light Source (ALS) is continuing. This major new research tool, which will occupy the historic site of the 184-inch cyclotron, will provide uniquely bright laser-like beams of x-ray and ultraviolet radiation. Its extremely high brightness and emission into very narrow spectral bands from undulator sources, as well as the broadband emission from bending magnets and wigglers, will make it a valuable tool for studying both the molecular and electronic structure of ceramics, polymers, metals, and alloys, not to mention its value to chemical sciences and biological sciences research. Although the Accelerator and Fusion Research Division is the lead division on the ALS, the new facility will open many research areas for MCS D investigators. Two related developments of particular interest are the Combustion Dynamics Facility, discussed below, and a new beamline to be constructed on the W13.6 wiggler at the ALS. The design and construction of this new beamline is being guided by a participating research team led by Philip Ross. This new beamline will be used by several MCS D research groups representing both materials and chemical sciences. MCS D research already planned for this beamline includes studies of the solid-liquid interface with x rays (P.N. Ross,

Investigator); *in situ* x-ray microscopy of ceramic materials (L.C. De Jonghe, Investigator, in collaboration with A. Thompson of the Center for X-Ray Optics); near-edge spectroscopy of actinide compounds (N. Edelstein and R. Andersen, Investigators); chemical physics at high photon energies (D.A. Shirley, Investigator); and surface spectroscopy in the extreme ultraviolet (to be led by a new ALS Professor, not yet appointed).

The Combustion Dynamics Facility (CDF) is a major new research initiative. The CDF is a joint LBL-Sandia National Laboratory (SNL) proposal for a national user facility established to advance DOE's energy sciences mission by enhancing the efficiency of the combustion process while minimizing undesirable effects such as the production of pollutants. The proposed facilities will be located at both LBL and SNL. Efforts at LBL will emphasize the underlying basic science, chemical dynamics, and the fundamental aspects of combustion chemistry, while efforts at SNL will emphasize complementary basic and applied research. A new building, the Chemical Dynamics Research Laboratory (CDRL), will house the proposed research facilities at LBL, which will include an infrared free-electron laser (IRFEL), advanced lasers, molecular-beam and surface apparatus, universal particle mass detectors, computation resources, and chemical physics beamlines connected to the ALS and optimized for chemical sciences research. Besides furthering basic science in chemical dynamics research, the CDF will also serve as a focus for developing advanced instrumentation for basic and applied research at the frontiers of understanding combustion chemistry and reaction dynamics processes. A close relationship between the basic research program and new user facilities at LBL and the more applied research program and complementary facilities at SNL will ensure a synergism that will speed the transfer of fundamental research to practical applications. Collaborations between staff and visitors at LBL and those at SNL will result in rapid development of optical diagnostics for polyatomic transient species that are critical in combustion processes. Construction of the project is estimated to take three and one-half years. The facility will begin operation in FY 1996 if funding starts in FY 1992.

A new "2%" initiative, Growth Mechanisms at Heterointerfaces, with Marjorie Olmstead as Investigator, was funded by DOE/BES/DMS at \$250k for FY 1990, a typical level of funding for one of these initiatives in the year preceding its formal start. In this project, the

formation and properties of complex thin-film heterostructures will be studied, in order to predict and fabricate systems with new or specifically tailored properties. Theoretical studies will be combined with complementary *in situ* characterization techniques. Two percent initiatives are chosen in a competition in which each DOE laboratory can enter two proposals, and they are funded from a pool of research money held back by DMS for new research that shows special promise. Full funding of \$700k is expected for FY 1991 and FY 1992.

The recent trend of a decline in the Division's DOE funds for most continuing programs continued during 1989 and is expected to remain the trend for the foreseeable future. The FY 1990 Materials Sciences base budget grew by 7.8% over the FY 1989 level, but much of the increase was earmarked for special purposes, including the 2% initiative, leaving an increase of 3.4% for continuing programs and "new starts." The Chemical Sciences budget decreased by 0.9% over the same period. These numbers are not adjusted for inflation, so we are steadily losing ground. The Division must face the probability of a continuing decline in the growth of DOE funding by maximizing the effective use of its scientific, technical, and financial resources, and by looking to other funding sources.

During 1989 Conway Peterson retired. Phil Ross was appointed Associate Division Director (ADD), and with that appointment, MCSD now has three scientists as ADDs, with somewhat separate scientific responsibilities between them. Phil Ross has become ADD for Materials Sciences research, Rolf Muller has become ADD for Chemical Sciences research, and Mark Alper continues as ADD for CAM. It is expected that this new structure will facilitate relations with DOE's Washington, D.C., offices.

As of October 1, 1989, there were a total of 657 MCSD staff: 89 investigators, 24 other staff scientists, 34 postdoctoral associates, 251 graduate students, 19 undergraduates, 38 administrative/clerical staff, 29 technical staff, and 173 guests. During the calendar year, 418 refereed journal articles were published by MCSD investigators. Students working with MCSD investigators received 13 M.S. and 62 Ph.D. degrees. The CAM activities are, as usual, covered in more detail in a separate Annual Report.

Honors received by MCSD investigators in calendar year 1989 include:

- Neil Bartlett was elected a Foreign Associate of the *Academie des Sciences* of France. He also received the Linus Pauling medal of the Pacific Northwest Section of the American Chemical Society.
- Mark Bednarski received the American Cancer Society Junior Faculty Research Award.
- Robert Bergman received the Edgar Fahs Smith Award of the Philadelphia Section of the American Chemical Society.
- Leo Brewer was elected a Fellow of the Advanced Materials Society International. He also received The Berkeley Citation from the University of California at Berkeley and was honored by the Leo Brewer Symposium on High-Temperature and Materials Chemistry, held at LBL.
- Lutgard de Jonghe received an Alexander von Humboldt Senior U.S. Scientist award.
- Heinz Heinemann received the Catalysis Club of Philadelphia award.
- Harold Johnston was appointed Faculty Research Lecturer at the University of California at Berkeley.
- Yuan Lee was named an External Scientific Member of the Max-Planck-Institute.
- William A. Lester received the Professional Achievement Award from the Northern California Council of Black Professional Engineers. He was also appointed to the General Office Commission on Nominations of the American Association for the Advancement of Science.
- Steven Louie received a Guggenheim fellowship.
- William Miller received the Langmuir Award in Chemical Physics.
- J.W. Morris received the AT&T Foundation Award of the Pacific Southwest Section of the American Society for Engineering Education.
- Rolf Muller was elected Chairman of the Physical Electrochemistry Division of the Electrochemical Society.
- Alexander Pines received the Pittsburgh Spectroscopy Award from the Spectroscopy Society of Pittsburgh.
- John Prausnitz received an honorary Doctor of Engineering degree from the University of Berlin.
- Robert Ritchie was named an Honorary Fellow of the International Congress on Fracture.
- Gerd Rosenblatt received a Dr. *honoris causa* degree in Physics from the Vrije Universiteit in Brussels.
- Richard Saykally received the E.K. Pyler Prize for Molecular Spectroscopy from the American Physical Society and the Bomem-Michelson Prize from the Coblentz Society.
- Glenn Seaborg was elected to the Engineering and Science Hall of Fame. He was also named an Honorary Member of the Royal Institution of Great Britain.
- Gabor Somorjai received the E.W. Mueller Award from the University of Wisconsin and was named an Alexander von Humboldt Senior U.S. Scientist.

- Andrew Streitwieser received the Arthur C. Cope Scholar Award from the American Chemical Society.
- Gareth Thomas was named the winner of the 1991 Albert Sauveur Achievement Award of the American Society of Metals.
- Peter Vollhardt was selected as the 1990 Lemieux Lecturer of the University of Ottawa.

Norman E. Phillips
Division Director
Materials and Chemical Sciences Division

METALLURGY AND CERAMICS

STRUCTURE OF MATERIALS

Structure and Properties of Transformation Interfaces*

Ronald Gronsky, Investigator

INTRODUCTION

The modern science of materials devotes increasing attention to the role of solid-state interfaces; they completely dominate the behavior of thin-film electronic devices, and they strongly influence the behavior of composite materials as well as bulk ceramic and metallic alloys. This program seeks a fundamental understanding of the role of interfaces in materials by applications of high-resolution electron microscopy to determine local interfacial structure and composition; by theoretical modeling to relate these parameters to actual atomic structure and composition; and by correlations with interfacial-specific properties, including conductivity, diffusivity, ductility, fracture toughness, mobility, and reactivity.

Significant attention has been given this past year to various interfaces in the new high- T_c superconducting materials. Planar defects, twins, and grain boundaries are examples of internal interfaces that act either as serious obstacles (e.g., "weak links") or as potential assets (e.g., flux-pinning sites) to the commercial implementation of these materials. The continued emphasis in this program is to understand interfacial atomic structure and transformation behavior.

1. Structural Defects and Electrical Properties of GaAs (Publications 1 and 2)

B.-T. Lee,[†] I.-S. Park,[‡] E. Bourret, and R. Gronsky

The behavior of As-related structural defects (dislocation loops and As precipitates) and the changes in EL2 concentration during bulk annealing of As-rich GaAs single crystals were studied in the temperature range of

500–900°C. Results show that the EL2 concentration increases and that some structural defects dissolve during bulk annealing above 600°C, indicating that the source of point defects necessary to form EL2 during bulk annealing is the excess As condensed during crystal growth in various forms. These included point defects, dislocation loops, and/or As precipitates, depending on the cooling rate from high temperatures and availability of heterogeneous nucleation sites, primarily dislocations. It was also determined that the solvus temperature for the crystal studied, with an excess As concentration of about $10^{16}/\text{cm}^3$, lies between 600 and 700°C.

The precipitates were identified as elemental rhombohedral As with a tetrahedral shape bounded by GaAs {111} planes, as shown in Figure 1-1. Some of the particles showed a simple orientation relationship with the matrix: all close-packed planes and directions were parallel.

Figure 1-1. High-resolution electron micrographs of two rhombohedral As precipitates in GaAs, showing the {111} GaAs lattice planes for scale. Emerging facets along the close-packed planes are evident even at this early developmental stage, accounting for the equilibrium tetrahedral shape eventually assumed by the particles. (XBL 884-2932)

*This work is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

This relation yields a high degree of structural coherence between the two phases and is responsible for the observed morphology. Other As precipitates associated with dislocations deviated from this simple orientation relationship by a few degrees, due to the strain field of the dislocation cores.

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[‡]Engineering Division, LBL.

2. Atomic Structure of Grain Boundaries in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{LaBaCaCu}_3\text{O}_{7-\delta}$ (Publication 3)

H.W. Zandbergen,[†] R. Gronsky, and G. van Tendeloo[‡]

High-resolution electron-microscopy studies of grain boundaries and fracture surfaces in both the tetragonal and orthorhombic phases of dense (>90%) $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{LaBaCaCu}_3\text{O}_{7-\delta}$ have been conducted to understand the reasons for the low critical current carried by these superconductors. Grain boundaries in polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ are found to be frequently parallel to a (001) plane of one of the adjacent grains, with a structure similar to that of the (001) free surface of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Matching of experimental and calculated images shows that the outermost surface layer in this compound is a deformed BaO layer. Both grain boundaries and fracture surfaces of $\text{LaBaCaCu}_3\text{O}_{7-\delta}$ show no such tendency for preferential orientation of the interface plane. The explanation for this difference lies in the fact that $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ transforms to its superconducting orthorhombic phase from a tetragonal precursor, while $\text{LaBaCaCu}_3\text{O}_{7-\delta}$ has no precursor phase. The precursor establishes the strong tendency for (001) grain-boundary planes in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ because of the 90° rotational mismatch of the three variants of the high-temperature tetragonal phase. Results indicate that the low critical currents observed in sintered materials are caused by this textured grain growth in combination with the atomic structure of the grain-boundary plane, and the intercalation of off-stoichiometric species near the grain boundary (see Figure 2-1).

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Figure 2-1. Micrograph of a grain boundary in dense $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ sintered at 950°C and annealed at 450°C, both treatments conducted for 48 hours in oxygen. The upper grain is approximately 10° off of an exact [110] orientation, and the lower grain is exactly in the [100] zone. The lower grain has only $(\text{CuO})_2$ double layers in the region near the grain boundary, indicating that it has changed in composition to the $\text{YBa}_2\text{Cu}_4\text{O}_{8-\delta}$ phase by consuming the solute available from within the boundary plane. Note the facets in the interface plane and the continuous bending of lattice planes in both grains. (XBB 888-7815)

3. Work In Progress

Continuing work is listed by thesis topic, followed by the graduate students responsible for the research: metallic contacts to $\text{YBa}_2\text{Cu}_3\text{O}_7$, M. Tidjani and M. Powers; grain-boundary structure in $\text{YBa}_2\text{Cu}_3\text{O}_7$, L. Yamamoto; epitaxy and structural defects in $\text{Ti}_2\text{Ca}_2\text{Ba}_3\text{Cu}_3\text{O}_{10}$ thin films, K. Atwal; structural transitions and effect of transition-metal doping in $\text{Bi}_2\text{SrCa}_2\text{Cu}_2\text{O}_{8+\delta}$ superconductors, K. Fortunati (work supported by DARPA through TCSUH); oxygen stoichiometry and phase transformations in $\text{YBa}_2\text{Cu}_3\text{O}_7$, M. Fendorf (work supported by DARPA through TCSUH); oxygen ordering and phase transitions in $\text{YBa}_2\text{Cu}_3\text{O}_7$, theory and experiment, C. Burmester (work supported by DARPA through TCSUH); corrosion susceptibility and grain boundaries in stainless steel, C. Willis; and multilayers for x-ray optical applications, T. Nguyen. In other projects, postdoctoral scientist Judith Ulan (NERC Fellowship) is investigating the microstructure of new zeolites in collaboration with S-Cal™ and Georgia Tech. Postdoctoral scientist Eric Kvam is studying both high- T_c superconductors and heteroepitaxy in various electronic materials.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. B.-T. Lee, E.D. Bourret, R. Gronsky, and I.S. Park, "Annealing of GaAs Single Crystals: Relationship Between Electrical Properties and Structural Defects," *J. Appl. Phys.* **65** 1030 (1989); LBL-25384.
2. B.-T. Lee, R. Gronsky, and E. Bourret, "Transmission Electron Microscopy Study of Arsenic Precipitates in GaAs: Morphology and Orientation Relationship with the Matrix," *J. Cryst. Growth* **96**, 333 (1989); LBL-26568.
3. H.V. Zandbergen, R. Gronsky, and G. van Tendeloo, "Atomic Structure of Grain Boundaries in $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ and $\text{LaBaCaCu}_3\text{O}_{7.8}$," *J. Superconductivity* **3**, 103 (1989); LBL-26397.

Other Publications

4. J. Ulan and R. Gronsky, "Effect of Alkali Cations on the Microstructure and Composition of Iron Silicate," in *Proc. 47th Annual Meeting Electron Microscopy Society of America*, G.W. Bailey, Ed., San Francisco Press, Inc., 1989, p. 268; LBL-26914.
5. K. Fortunati, M. Fendorf, M. Powers, C. Burmester, and R. Gronsky, "Preparation of BiCaSrCuO Specimens for High Resolution Transmission Electron Microscopy," in *Proc. 47th Annual Meeting Electron Microscopy Society of America*, G.W. Bailey, Ed., San Francisco Press, Inc., 1989, p. 714; LBL-26916.
6. T. Nguyen, R. Gronsky, and J. Kortright, "Detection of Crystalline Phase in Cross-Section Multilayer Thin Film by High Resolution Transmission Electron Microscopy," in *Proc. 47th Annual Meeting Electron Microscopy Society of America*, G.W. Bailey, Ed., San Francisco Press, Inc., 1989, p. 680; LBL-27095.

LBL Reports

7. C.J.D. Hetherington, E.C. Nelson, K.H. Westmacott, R. Gronsky, and G. Thomas, "The Berkeley Atomic Resolution Microscope—an Update," in *Proc. MRS Fall 1988 Meeting* (in press); LBL-25797.
8. R. Csenesits and R. Gronsky, "Vitrification of Zeolite Y in the TEM," *Zeolites* (in press); LBL-22549.
9. H.W. Zandbergen, R. Gronsky, and G. Thomas, "The Atomic Structure at Grain Boundaries, the Cause of Low Critical Currents in Sintered $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$," in *Proc. EUREM Congress*, York, U.K., Sept. 1988 (in press); LBL-25800.
10. T. Nguyen, J. Kortright, and R. Gronsky, "High Resolution Studies of Tungsten-Carbon Multilayers," in *Proc. MRS Fall 1989 Meeting* (in press); LBL-25901.
11. C. Burmester, L.T. Wille, and R. Gronsky, "In-Situ Transmission Electron Microscopy and Computer Simulation Study of the Kinetics of Oxygen Loss in

$\text{YBa}_2\text{Cu}_3\text{O}_x$," in *Proc. MRS Fall 1989 Meeting* (in press); LBL-27358.

12. K. Fortunati, R. Gronsky, R.L. Meng, and C.W. Chu, "Transmission Electron Microscopy Study of Fe-doped BiCaSrCuO ," in *Proc. MRS Fall 1989 Meeting* (in press); LBL-27462.
13. K.P. Atwal, R. Gronsky, J. Nickel, A. Markelz, and D.E. Morris, "A Study of the Thermodynamic Stability of $\text{YBa}_2\text{Cu}_4\text{O}_8$," in *Proc. MRS Fall 1989 Meeting* (in press); LBL-27469.
14. E. Kvam, D.M. Maher, and C.J. Humphreys, "Dislocation Behavior in $\text{Ge}_x\text{Si}_{1-x}$ Epilayers on (001) Si," in *Proc. MRS Fall 1989 Meeting* (in press); LBL-28096.
15. R. Gronsky, "Atomic Resolution Microscopy," in *Images of Materials*, R. Gronsky, A.R. Pelton, and D.B. Williams, Eds., Oxford University Press, 1989 (in press); LBL-25822.
16. R. Gronsky, "Interfacial Structure and Properties in High T_c Superconductors," in *Symposium on "Structure and Properties of Fine and Ultrafine Particles, Surfaces & Interfaces"*, TMS Fall Meeting, Indianapolis, IN, Oct. 1, 1989 (in press); LBL-27193abs.
17. R. Gronsky, "Observation of Ledges with Atomic Resolution TEM," in *Symposium on "The Role of Ledges in Phase Transformations"*, TMS Fall Meeting, Indianapolis, IN, Oct. 1, 1989 (in press); LBL-27194abs.

Invited Talks

18. R. Gronsky, "From Metals to Ceramics: A (Short) History of Superconductivity," ASME Northern California Section Meeting, Berkeley, CA, Jan. 25, 1989.
19. R. Gronsky, "Grain Boundary Structure and J_c in High T_c Superconductors," TMS Annual Meeting, Symposium on High Temperature Superconducting Oxides, Las Vegas, NV, Feb. 27–Mar. 3, 1989.
20. R. Gronsky, "Atomic Imaging of Defects in Si and GaAs," Eleventh Annual Industrial Liaison Conference, Berkeley, CA, Mar. 15–16, 1989.
21. R. Gronsky and T.E. Mitchell, Conference Organizers, Symposium on High Temperature Superconductivity, Scanning 89/EM West, Apr. 5–7, 1989.
22. R. Gronsky, "TEM Imaging of Magnetic Materials," DOE Council of Materials Sciences Panel on Magnetism at Surfaces and Interfaces, Santa Fe, NM, June 17–21, 1989.
23. R. Gronsky, M. Fendorf, K. Fortunati, C. Burmester, and M. Powers, "Characterization of Microstructure and Local Atomic Environment in Transition-Metal Doped BCSCO Superconductors," DARPA First Annual High Temperature Superconductors Workshop, Engineering, UCSB, Sept. 11–14, 1989.
24. R. Gronsky, "Future of High Resolution Electron Microscopy," at "Higgs Meeting," Presqu'île de Giens, France, Sept. 22–27, 1989.
25. R. Gronsky, "Observation of Ledges with Atomic Resolution TEM," Symposium on Role of Ledges in

- Phase Transformations, TMS Fall Meeting, Indianapolis, IN, Oct. 1-5, 1989.
26. R. Gronsky, chair of panel discussion on "Experimental Distinction Between Ledges and Dislocation with TEM," panelists W.M. Stobbs and R. Bonnet, Symposium on Role of Ledges in Phase Transformations, TMS Fall Meeting, Indianapolis, IN, Oct. 1-5, 1989.
27. R. Gronsky, "Interfacial Structure and Properties in High T_c Superconductors," Symposium on Structure and Properties of Fine and Ultrafine Particles, Surfaces and Interfaces, TMS Fall Meeting, Indianapolis, IN, Oct. 1-5, 1989.

Microstructure, Properties, and Alloy Design: Inorganic Materials*

Gareth Thomas, Investigator

INTRODUCTION

This is a multicomponent, interdisciplinary program in advanced inorganic materials involving fundamental quantitative studies of the structure-property relationships in technologically significant materials involved in energy and conservation. All tasks involve characterization of both structure and composition at the highest levels of spatial (transmission electron microscopy) and chemical (spectroscopy) resolution in order to understand the complexities of structure-composition-processing-property relationships, without which alloy design is impossible. Specific tasks include (a) magnetic materials: ceramics, and permanent and rare earth magnets; and (b) high-critical-temperature superconducting ceramics.

The overall objectives are to understand structure-property relations so as to improve performance, e.g., by microstructural design of new materials, or to better utilize existing materials and processing routes for industrial practice and to realize materials and energy conservation.

The steel alloy development program has now been terminated. Half a dozen patents have been issued, and attempts to transfer the technology to industry will continue. It is important to reiterate what was stated last year: research interest by students in ferrous metallurgy has rapidly declined, especially by U.S. students, in recent times. We have a manpower shortage in the metallurgical industries that is continuing to become a severe national problem now that many foreigners return to their home countries, especially Korea and the Republic of China.

1. Structural Imaging of Polytypoids in High- T_c Oxide Superconductors (Publication 16)

R. Ramesh, E. Wang,[†] J.M. Tarascon,[†] and G. Thomas

The structure of the superconducting polytypoid in the newly discovered high- T_c superconducting system $Pb_2Sr_2(Ca,Y)Cu_3O_y$ has been examined by high-resolution electron microscopy, electron diffraction, and x-ray

microanalysis. High-resolution imaging has shown the presence of $Pb_2Sr_2Cu_2O_y$ at the grain boundaries. By analogy to the Bi-Ca-Sr-Cu-O (BCSCO) system, it is suggested that this polytypoid could have a lower transition temperature compared to the matrix. This finding may explain the steps in the resistivity plot. It is also shown that complex cationic ordering, such as replacement of Sr by Ca and/or Y, could lead to extra reflections in the diffraction patterns.

Pb-Sr-(Ca-RE)-Cu-O sintered samples (where RE is rare earth) were prepared by standard solid-state processing techniques. High-resolution electron microscopy (HREM) was carried out at 800 kV on the Atomic Resolution Microscope at LBL's National Center for Electron Microscopy (NCEM). Analytical electron microscopy and electron diffraction were carried out using a JEOL 4000FX at 400 kV. X-ray microanalysis and quantification were carried out using a Tracor Northern System.

Figure 1-1 shows a HREM image of the matrix phase in the [100] zone-axis orientation. The cationic stacking sequence in this image consists of two layers of PbO between which is located a Cu atom in the +1 state (as identified by XPS studies). Between the PbO bi-layers, the stacking sequence consists of Sr-Cu-(Ca,Y)-Cu-Sr repeat units. One difference from the BCSCO system is the fact that there is no glide plane between the PbO layers, so that the repeat unit along the c-direction is only 15.76 Å (instead of double that). Figure 1-2 shows the stacking sequence adjacent to a grain boundary. In this case the last unit cell at the grain boundary corresponds to $Pb_2Sr_2Cu_2O_y$, which, by analogy to the BCSCO system, may be a superconductor

Figure 1-1. [100] zone-axis HREM image of the superconducting phase of the newly discovered high- T_c system with the composition $Pb_2Sr_2(Ca,Y)Cu_3O_y$. (XBB 902-1728)

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Figure 1-2. [110] zone-axis image of the superconducting phase of the material shown in Figure 1-1, showing the formation of one unit cell of $\text{Pb}_2\text{Sr}_2\text{Cu}_2\text{O}_y$ adjacent to the grain boundary. (XBB 902-1229)

with a low T_c , or even a semiconductor. This conclusion correlates well with the resistivity plot, which exhibits an onset at 60 K, while T_{c0} is obtained only at 20 K.

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2. Electron Microscopy of a Gd-Ba-Cu-O Superconductor (Publication 4)

R. Ramesh, G. Thomas, R.L. Meng,[†] P.H. Hor,[†] and C.W. Chu[†]

An electron microscopy study has been carried out to characterize the microstructure of a sintered Gd-Ba-Cu-O superconductor alloy. The $\text{GdBa}_2\text{Cu}_3\text{O}_{7-x}$ phase in the oxygen-annealed sample is orthorhombic, while in the vacuum-annealed sample it is tetragonal. The details of the fine structure in the [001] zone-axis convergent-beam patterns can be used to distinguish between the orthorhombic form and the tetragonal form. In addition to this matrix phase, an amorphous phase is frequently observed at the triple grain junctions. Gd-rich inclusions have been observed inside the matrix phase. An example is shown in Figure 2-1.

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Figure 2-1. Top: [001] zone-axis convergent-beam electron diffraction (CBED) pattern from the orthorhombic, twinned matrix phase, depicting the 2-mm diffraction group symmetry; bottom: [001] zone-axis CBED pattern from the domain adjacent to that from which the top CBED pattern was obtained. (XBB 902-1230)

3. Improvement in Intrinsic Coercivity of Sintered Fe-Nd-B Magnets by the Introduction of Nonmagnetic Dispersoids (Publication 2)

R. Ramesh, G. Thomas, and B.M. Ma[†]

The microstructure of Ho-substituted sintered Fe-Nd-B magnets, prepared by two different routes, has been characterized in order to understand the changes in intrinsic coercivity with Ho content. Spherical inclusions in the size

range of 500 Å–1 μm have been observed inside the matrix RE₂Fe₁₄B grains. Characterization by x-ray diffraction, electron microdiffraction, and energy-dispersive x-ray microanalysis shows that these inclusions are fcc rare-earth oxides. The volume fraction of these inclusions increases with Ho content. Ho partitions preferentially into the matrix phase, and no segregation of Ho to the interphase interfaces is observed. Lorentz electron microscopy experiments suggest that the inclusions in the lower end of the size distribution are capable of pinning the magnetic domain walls, and hence these nonmagnetic inclusions must contribute to the increase in intrinsic coercivity.

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4. Microstructure of Melt-Spun Nd-Fe-Co-B Magnets (Publication 6)

C. Koestler, R. Ramesh, C.J. Echer,[†] G. Thomas, and J. Wecker[†]

This paper describes the microstructural characterization of melt-spun Nd₁₇Fe₇₇B₆ and Nd₁₅(Fe_{1-x}Co_x)₇₇B₈ ribbons using high-resolution electron microscopy, x-ray microanalysis, and microdiffraction. In general, the microstructure consists of the hard magnetic Nd₂Fe₁₄B phase and one or more grain-boundary phases (see Figure 4-1). In all these materials, no Nd₁₁Fe₄B₄ phase was observed. The grain-boundary phase in the Co-free samples appears mainly at multigrain junctions and is a Nd-rich, crystalline (fcc) phase, whereas the Co-containing specimens comprise two different fcc grain-boundary phases. The structural and microchemical data (see Figure 4-2) indicate that these are likely to be ferromagnetic and that they contain significantly less Nd than the grain-boundary phase of the Co-free samples. The average matrix grain diameter is about 80 nm, but there are always some areas in every specimen where the grain diameter is very small (about 20 nm) or very large (more than 300 nm), causing differences in the size of the grain-boundary phases both at the triple grain junctions and between the grains.

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Figure 4-1. Bright-field images of areas with 40 nm (a), 100 nm (b), and more than 300 nm (c) average matrix grain size in a Nd₁₅(Fe_{0.7}Co_{0.3})₇₇B₈ sample. (XBB 880-9692)

Figure 4-2. EDX spectra of the $\text{Nd}_2(\text{Fe}_{0.7}\text{Co}_{0.3})_{14}\text{B}$ matrix phase (a), the $\text{Nd}_{20}(\text{Fe}_{0.7}\text{Co}_{0.3})_{80}$ fcc grain-boundary phase (b), and of the $\text{Nd}(\text{FeCo})_2$ fcc grain-boundary phase (c). Boron is not detectable by a Be window EDX detector. The small Cl peak in (c) is due to etching the constituents with HCl prior to melting. (XBL 8810-3573)

5. Dy-Al Sintering Additive: Effect on Microstructure and Magnetic Properties of Fe-Nd-B Magnets (Publication 11)

R. Ramesh, G. Thomas, and B.M. Ma[†]

The effect of a Dy-4wt% Al eutectic sintering additive to a Fe-Nd-B alloy has been studied. As shown in Figure 5-1, large increases in the iH_c have been obtained for additions of above 4%, along with energy products in the range of

Figure 5-1. (a) Remanence as a function of wt% of sintering aid, Dy-4%Al; (b) intrinsic coercivity as a function of Dy-Al content; (c) energy product as a function of Dy-Al content. (XBL 902-491)

27–38 MGOe, thus making these alloys potential candidates for applications involving temperatures higher than ambient. The microstructural studies show that there is a significant uniform segregation of Al to the matrix-fcc phase interface, while Dy appears to segregate weakly. The overall microstructure is similar to that of the ternary alloys, and the magnetization-reversal mechanism is also similar to that of the ternary alloys, i.e., nucleation-type. Further experimentation is required in order to optimize the composition and processing conditions so that the required composition profiles are achieved.

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6. Control Rolling and Cooling for On-Line Production of Strong, Tough Steels (Publication 10)

G. Thomas

Strong, tough steels have been designed to produce microcomposite structures of fine-grained auto-tempered lath martensite with untransformed austenite films between the laths. Such structures can be produced on-line in a hot

mill by controlled rolling and cooling. The steels are based on Fe/Cr/Mn/C compositions that can be air hardenable, or for lean composition, water-quench hardened with Nb microalloying. The latter steels can also be processed on-line in a modern plate plant with water cooling at $\sim 30^\circ\text{C}/\text{sec}$ (see Figure 6-1). The steels have excellent mechanical properties that are superior to current HSLA steels (see Figures 6-2 and 6-3), and they require no subsequent heat treatment following rolling and cooling.

7. Work in Progress

Hard Magnets

Work is continuing on the correlation of microstructure, composition, processing, and magnetic properties of the hard, high-energy-product magnets. Continued work on iron-boron-neodymium-based permanent magnets involves post-sintering isothermal heat treatments so as to modify the distribution of the alloying additions and the grain-boundary microstructure. The general microstructure consists of large tetragonal $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains, with fcc NdO and occasionally hcp Nd_2O_3 existing at grain boundaries and multigrain junctions. Inclusions containing up to 10 at% Dy were also observed at multigrain junctions. The energy product $(BH)_{\text{max}}$ and the coercivity decrease from greater than 50 MGOe and 25 kOe for the as-sintered condition to 46 MGOe and 18 kOe, respectively, as a consequence of the heat treatment. Results of microstructural characterization revealed no discernible differences as a consequence of the heat treatments that could explain the decrease in magnetic

Figure 6-1. Schematic showing processing routes for on-line production of microcomposite steels. (XBL 8810-3730)

Figure 6-2. Summary of data for Charpy properties of QT steels. (XBL 859-6624)

Figure 6-3. Summary of data for K_{IC} properties of QT steels. (XBL 859-6625A)

properties. It is therefore suggested that the quenching stresses are responsible for the deterioration. An optimal microstructure for nucleation-controlled permanent magnets is proposed.

Microstructure of mechanically alloyed Nd₁₆Fe₇₆B₈ magnets (collaboration with L. Schulz, Siemens AG Research Laboratories, Erlangen, Federal Republic of Germany). High-resolution electron microscopy and analytical electron microscopy are being used to characterize mechanically alloyed isotropic and anisotropic Nd₁₆Fe₇₆B₈ magnets. In both samples, two rare-earth oxide phases, NdO and Nd₂O₃, and a boron-rich phase have been observed. Two grain-boundary phases, the NdFe₂ phase and a nonequilibrium Nd-rich phase, were found only in the isotropic samples and seem to be responsible for their higher coercivity. Due to the alignment of the grains, the anisotropic materials possess a better squareness of the B-H loop and a higher energy product. Thus the magnetic characteristics of these alloys (nucleation or pinning or both) depend critically on the processing conditions.

Microstructure of mechanically alloyed Fe₇₈Mo₁₀Sm₁₂ magnets with the ThMn₁₂ structure (in collaboration with L. Schultz, Siemens AG Research Laboratories, Erlangen, Federal Republic of Germany). Mechanically alloyed ThMn₁₂-type Fe₇₈Mo₁₀Sm₁₂ magnets are being characterized by high-resolution electron microscopy, x-ray microanalysis, and microdiffraction. In general, the microstructure of the mechanically alloyed and annealed magnets consists of the tetragonal 1:12 matrix phase with an average matrix grain diameter of 200–300 nm and two RE-oxide phases, the SmO phase and the Sm₂O₃ phase, which was found to exist only in a single-crystal hcp and monoclinic structure. In this material, no grain-boundary phases at multigrain junctions were observed. The high defect concentration in the matrix grains seems to be responsible for pinning of the domain walls and good magnetic properties of the Fe₇₈Mo₁₀Sm₁₂ magnets. However, so far it has not been possible to resolve magnetic domains by Lorentz imaging methods.

Microstructure-Property Relationships in High-T_c Ceramics

This research involves high-resolution electron microscopy and spectroscopy studies of alkaline-earth and rare-earth superconducting oxide ceramics and correlation with physical properties.

Bi-Ca-Sr-Cu-O (+Pb) compounds. We are currently investigating the microstructure in BiCaSrCuO superconducting specimens and correlating the results with the processing conditions and electrical properties. These compounds form a series of polytypoid structures, each with a specific critical temperature. In particular, since the oxygen content in BiCaSrCuO is thought to play an important role in the structure and properties, current and future work involves the investigation of post-anneal treatments under varying partial pressures of oxygen. A preliminary high-resolution electron-microscope investigation has shown that severe degradation of the microstructure occurs for oxygen partial pressures that are higher or lower than the optimal pressure. Specifically, the $n = 3$ type polytypoid reverts to the $n = 2$ type polytypoid, and there is a corresponding deterioration in electric properties. (T_c drops from ~115 K to 85 K.) The samples are prepared by Dr. S. Green of the Center for Superconductivity, University of Maryland, who also does the electrical characterization. The structural characterization is performed on the ARM-1000 at NCEM.

Y-Ba-Cu-O thin films. A collaborative research program between NCEM, LBL, and Bellcore has been initiated to investigate the structural and microstructural details of thin films of Y-Ba-Cu-O. As part of this program, Dr. R. Ramesh from Bellcore visits NCEM as an external user of the Center's facilities. We have observed a new phase in the Y-Ba-Cu-O system with the cationic stoichiometry of "224" (as compared to YBa₂Cu₃O₇, which is termed as "123"). This structure has been found only as defects in a film of nominal composition, equal to "123." The thin films also exhibit frequent intergrowths of the "248" structure. In addition, polytypoidic superlattices have also been observed in the thin films. It is planned to attempt to synthesize and characterize the "224" phase in collaboration with Dr. S.M. Green (Center for Superconductivity Research, University of Maryland) and Dr. Ramesh (Bellcore).

Y-Ba-Cu-O bulk ceramics. Another aspect that will be focused upon is the attainment of high critical currents in bulk "123" materials. The results obtained on thin films reveal that it may be possible to tailor the microstructure of the sintered samples in order that high intragranular critical currents be obtained. As in the case of thin films, it is essential to pin the fluxons inside each grain. One novel method to achieve this is to form the "248" structure and heat-treat it under suitable conditions in order to decompose it to the "123" phase plus CuO. It is hoped that the CuO will form a coherent lamellar precipitate inside grains of the "123" phase.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. R. Ramesh, G. Thomas, S.M. Green, M.L. Rudee, Y. Mei, and H.L. Luo, "Bi-Ca-Sr-Cu-O Superconductors: The Connectivity Issue," *IEEE Trans. Magn.* **25**, 2360 (1989); LBL-25842.
2. R. Ramesh, G. Thomas, and B.M. Ma, "Improvement in Intrinsic Coercivity of Sintered Fe-Nd-B Magnets by the Introduction of Non-Magnetic Dispersoids," *Acta Metall.* **37**, 1421 (1989); LBL-25648.
3. H.M. Ho, C. Gau, and G. Thomas, "Domain Structure and Microstructure of Co-Ni Oblique Incidence Thin Films," *J. Appl. Phys.* **65**, 3161 (1989); LBL-25914.[†]
4. R. Ramesh, G. Thomas, R.L. Meng, P.H. Hor, and C.W. Chu, "Electron Microscopy of a Gd-Ba-Cu-O Superconductor," *J. Mater. Res.* **4**, 515 (1989); LBL-25405.
5. L.H. Chan, G. Thomas, and J.S. Gau, "Magnetic Properties and Microstructure of Co-Cr Bulk Alloys," *J. Magn. Magn. Mater.* **79**, 95 (1989); LBL-25266.^{*}
6. C. Koestler, R. Pamesh, C.J. Echer, G. Thomas, and J. Wecker, "Microstructure of Melt Spun Nd-Fe-Co-B Magnets," *Acta Metall.* **37**, 1945 (1989); LBL-26156.
7. R. Ramesh and G. Thomas, "Interrelationships between Structure and Property in Magnetic Materials," *Mat. Sci. & Eng. J. B3*, 435 (1989); LBL-27827.
8. R.S. Rai, M.A. O'Keefe, and G. Thomas, " $\delta_2\text{Y}_2\text{Si}_2\text{O}_7$ Structure Confirmed by Processing and Simulation of Atomic-Resolution Images," *Mat. Res. Soc. Symp. Proc.* **139**, 175 (1989); LBL-16336.
9. C.J.D. Hetherington, E.C. Nelson, K.H. Westmacott, R. Gronsky, and G. Thomas, "The Berkeley Atomic Resolution Microscope—An Update," *Mat. Res. Soc. Symp. Proc.* **139**, 277 (1989); LBL-25797.

Other Publications

10. G. Thomas, "Control Rolling and Cooling for On-Line Production of Strong, Tough Steels," in *Modernization of Steel Rolling*, Proc. of ICMSR '89, Beijing, People's Republic of China, 1989, p. 63; LBL-26208.
11. R. Ramesh, G. Thomas, and B.M. Ma, "Dy-Al Sintering Additive: Effect on Microstructure and Magnetic Properties of Fe-Nd-B Magnets," in Conf. Proc. MRS Intl. Mtg., Tokyo, Japan, *Microstructure-Property Relations in Magnetic Materials*, **11**, 35 (1989); LBL-24401.
12. T. Huynh and G. Thomas, "Characterization of Barium Ferrite Recording Materials," in Conf. Proc. MRS Intl. Mtg., Tokyo, Japan, *Microstructure-Property Relations in Magnetic Materials*, **11**, 229 (1989); LBL-25359.
13. J.D. Kim and G. Thomas, "Microstructural and Magnetic Characterization of Fe-Si-Al (Sendust) Alloys," in Conf. Proc. MRS Intl. Mtg., Tokyo, Japan, *Microstructure-Property Relations in Magnetic Materials*, **11**, 223 (1989); LBL-25362.
14. T.A. Epicier and G. Thomas, "Conditions for Atomic Imaging of Mullite," in *Proc. 47th Annual EMSA Meeting*, San Antonio, TX, G.W. Bailey, Ed., 1989, p. 418; LBL-26893.
15. T.A. Epicier, H. Wohlfromm, and G. Thomas, "Dislocation Analysis in Al_2TiO_5 ," in *Proc. 47th Annual EMSA Meeting*, San Antonio, TX, G.W. Bailey, Ed., 1989, p. 422; LBL-26894.
16. R. Ramesh, E. Wang, J.M. Tarascon, and G. Thomas, "Structural Imaging of Polytypoids in High T_c Oxide Superconductors," in *Proc. 47th Annual EMSA Meeting*, San Antonio, TX, G.W. Bailey, Ed., 1989, p. 156; LBL-26915.
17. G. Thomas, "High Voltage High Resolution Electron Microscopy," in Conf. Proc. *ATTI del XVII Congress de Microscopie Elettronica*, Lecce, Italy, 1989, p. 13.
18. G. Thomas, "Atomic Imaging of Inorganic Materials," in Conf. Proc. *III Balkan Congress on Electron Microscopy*, Athens, Greece, 1989, p. 178.
19. G. Thomas, "Characterization of Advanced Ceramic Materials by Electron Microscopy," in Proc. 1st Japan Intl. SAMPE Symp., *New Materials and Processes for the Future*, N. Igata, I. Kimpura, T. Kishi, E. Nakata, A. Okura, and T. Uryu, Eds., 1989, p. 857; LBL-27244.
20. G. Thomas, "High Resolution Electron Microscopy and Microanalyses of Ferrites and Cuprates," in Conf. Proc. 5th Intl. Conf. on Ferrites, Bombay, India, *Advances in Ferrites*, C.M. Srivastava and M.J. Patni, Eds., Vol. 1, 1989, p. 197; LBL-26626.
21. H. Wohlfromm, P. Pena, J.S. Moya, A.P. Tomsia, and G. Thomas, "Joining of Aluminum Titanate with Niobium," in *Proc. 1st European Ceramic Society Conf.*, Maastricht, The Netherlands, June 18–23, 1989.[†]
22. M.K. Cinibulk (M.S. Thesis), "Processing of Silicon Nitride Ceramics for Improved High Temperature Performance."[†]
23. D.L. Callahan (Ph.D. Thesis), "Metal-Ceramic Bonding in Dicalcium Silicate Composites with Ni."[†]
24. R. Ramesh and G. Thomas, "High Energy Product Permanent Magnet Having Improved Intrinsic Coercivity and Method of Making Same," patent filing, DOE Ref. No. S-67519, pending 1989.
25. G. Thomas, S.M. Johnson, and T.R. Dinger, "Method of Producing a Dense Refractory Silicon Nitride (Si_3N_4) Compact with One or More Crystalline Intergranular Phases," U.S. Patent 4,830,800.[†]
26. C. Koestler, L. Schultz, and G. Thomas, "Microstructure of Mechanically Alloyed $\text{Fe}_{78}\text{Mo}_{10}\text{Sm}_{12}$ Magnets with Thin Film Mn_{12} Structure," *J. Appl. Phys.* (in press); LBL-28062.
27. R. Ramesh, D.M. Hwang, T.S. Ravi, A. Inam, I. Nasor, X. Dilla, T. Venkatesan, G. Thomas, A.F. Marshall, and T.H. Geballe, "Direct Observation of Structural Defects in Thin Film Y-Ba-Cu-O Superconductor," *Science* (in press); LBL-27678.

LBL Reports

26. C. Koestler, L. Schultz, and G. Thomas, "Microstructure of Mechanically Alloyed $\text{Fe}_{78}\text{Mo}_{10}\text{Sm}_{12}$ Magnets with Thin Film Mn_{12} Structure," *J. Appl. Phys.* (in press); LBL-28062.
27. R. Ramesh, D.M. Hwang, T.S. Ravi, A. Inam, I. Nasor, X. Dilla, T. Venkatesan, G. Thomas, A.F. Marshall, and T.H. Geballe, "Direct Observation of Structural Defects in Thin Film Y-Ba-Cu-O Superconductor," *Science* (in press); LBL-27678.

28. T. Epicier, M.A. O'Keefe, and G. Thomas, "Atomic Imaging of 3:2 Mullite," *Acta Crystallogr.* (in press); LBL-27169.[†]
29. R. Ramesh, N.J. Kim, and G. Thomas, "Improvement in Toughness of Fe-Cr-Mn-C Steels by Thermal-Mechanical Treatments," *Metall. Trans.* (in press); LBL-26866.
30. C. Koestler, M. Chandramouli, G. Thomas, and L. Schultz, "Microstructure of Mechanically Alloyed Nd₁₆Fe₁₆B₈-Magnets," submitted to *J. Magn. Magn. Mater.*; LBL-28260.
31. G. Thomas, "Characterization of Advanced Materials by Electron Microscopy," in *Proc. 12th ICXOM Congress*, Cracow, Poland, Aug. 28–Sept. 1, 1989 (in press); LBL-27245.
32. C.J.D. Hetherington and G. Thomas, "Atomic Imaging and Interfacial Analysis," *Acta Metall.* (in press); LBL-26734.
33. K.C. Lin (M.S. Thesis), "Microstructure and Magnetic Properties of CoNiCr/Cr Thin Film Disks," LBL-27741.
34. R. Ramesh, S.M. Green, and G. Thomas, "Microstructure Property Relationships in the Bi(Pb)-Sr-Ca-Cu-O Ceramic Superconductors," in *Studies of High Temperature Superconductors*, A. Narlikar, Ed., Nova Science (in press); LBL-27829.
35. R. Ramesh, C. Koestler, and G. Thomas, "Physical Metallurgy of Fe-Nd-B Magnets," ASM Fall Meeting, Indianapolis, IN, 1989; LBL-27216abs.
43. G. Thomas, "Developments in Processing for Rolled Steel Products," Pohang Steel Co., Seoul, Republic of Korea, Jan. 4, 1989.
44. G. Thomas, "High Resolution Electron Microscopy of Ferrites and Cuprates," 5th International Ferrite Conference, Bombay, India, Jan. 10–15, 1989.
45. R. Ramesh, T. Thomas (presenter), C. Salling, and S.C. Schultz, "Microstructure of γ -Fe₂O₃ Prepared by Forced Hydrolysis of Ferric Salts," 5th International Ferrite Conference, Bombay, India, Jan. 10–15, 1989; LBL-25662.
46. R. Ramesh, C.J.D. Hetherington, G. Thomas (presenter), S.M. Green, and H.L. Luo, "Transmission Electron Microscopy of High T_c Bi-Ca-Sr-Cu-O Superconductor," 5th International Ferrite Conference, Bombay, India, Jan. 10–15, 1989; LBL-25661.
47. C. Hetherington and G. Thomas, "Atomic Imaging and Interfacial Analysis," *Acta/Scripta Metallurgica Conference on Bonding, Structure and Mechanical Properties of Metal/Ceramic Interfaces*, University of California at Santa Barbara, Jan. 16–19, 1989.
48. G. Thomas, "Electron Microscopy and Microanalysis of Fine Ceramics," Mitsubishi Mining and Cement Co., Chichibu, Japan, Feb. 20, 1989.
49. G. Thomas, "Electron Microscopy and Microanalysis of Magnetic Materials," Showa Denko K.K. Co., Tokyo, Japan, Feb. 21, 1989.
50. G. Thomas, "Grain Boundaries in Ceramics," China Steel Corp., Kaohsiung, Republic of China, Feb. 23, 1989.
51. G. Thomas, R. Ramesh, S.M. Green, and H.L. Luo, "Transmission Electron Microscopy of High T_c BSSCO Superconductors," TMS-AIME Spring Meeting, Las Vegas, NV, Feb. 28–Mar. 1, 1989.
52. G. Thomas, C. Koestler, R. Ramesh, C.J. Echer, and J. Wecker, "Microstructure of Melt Spun Fe-Co-Nd-B Magnets," TMS/AIME Spring Meeting, Las Vegas, NV, Feb. 28–Mar. 1, 1989.
53. G. Thomas, "Transmission Electron Microscopy: Imaging of Materials," plenary lecture, International Conference on Scanning Electron Microscopy West, Long Beach, CA, Apr. 4–7, 1989.
54. G. Thomas, "Control Rolling and Cooling for On-Line Production of Strong, Tough Steels," plenary lecture, ICMSR 89, Beijing, People's Republic of China, Apr. 10–15, 1989.
55. G. Thomas, "Generic Microstructures in Structural and Electronic Ceramics," Allied Signal Co., Morristown, NJ, Apr. 21, 1989.
56. L. Sidjanin (presenter), S. Miyasato, and G. Thomas, "Microstructure-Drawing Limit Relations on Dual-Phase High Strength Steel Wire," 6th Scientific Meeting, International Symposium on Plasticity and Resistance to Metal Deformation, Herceg Novi, Yugoslavia, Apr. 26–28, 1989.
57. T.R. Dinger (presenter), G. Thomas, M.K. Cinibulk, and S.M. Johnson, "Crystallization Behavior of a Glass in the Y₂O₃-SiO₂-AlN System," Ceramic Society Conference, Tenerife, Spain, May 1989.

Invited Talks

36. C. Koestler, R. Ramesh, G. Thomas, L. Schultz, and J. Wecker, "Microstructure of High Coercivity Fe-Sm-Mo Mechanically Alloyed Magnets," Intermag '89 Conference, Washington, DC, Mar. 28–31, 1989.
37. M. Chandramouli, R. Ramesh, and G. Thomas, "Microstructure of Fe-Nd-B Magnets with Dy-Al Additions," Intermag '89 Conference, Washington, DC, Mar. 28–31, 1989.
38. K.C. Lin, H.M. Ho, T. Lin, J.S. Gau, and G. Thomas, "Effect of Cr Thickness on Microstructure, Magnetic Properties and Recording Characteristics of Cr-Ni Cr/Cr Hard Disks for Longitudinal Recording," Intermag '89 Conference, Washington, DC, Mar. 28–31, 1989.[†]
39. T.R. Dinger, G. Thomas, M.K. Cinibulk, and S.M. Johnson, "Crystallization Behavior of a Glass in the Y₂O₃-SiO₂-AlN System," Ceramic Society Conference, Tenerife, Spain, May 1989.[†]
40. K.C. Lin, G. Thomas, T. Lin, and J.S. Gau, "Effect of Media Properties on Side Erase Bands," M.R.M. '89 Conference, Rimini, Italy, Sept. 4–6, 1989.[†]
41. C. Koestler, G. Thomas, and L. Schultz, "Microstructure of Mechanically Alloyed Fe₇₆Nd₁₆B₈ Permanent Magnets," Conf. Elektronenmikroskope, Salzburg, Austria, Sept. 10–16, 1989; LBL-27056abs.
42. D. Callahan, G. Thomas, J.S. Moya, and P. Pena, "Reaction Sintering of C₂S-CZ Ceramics," 91st Annual Meeting, American Ceramic Society, Indianapolis, IN, Apr. 23–27, 1989.[†]

58. G. Thomas, "Characterization of Inorganic Materials," College of Engineering Industrial Liaison Trip, Mitsubishi Mining and Cement Co., Tokyo, Japan, May 29, 1989.
59. G. Thomas, "Electron Microscopy and Microanalysis of Structural Ceramics," College of Engineering Industrial Liaison Trip, Tosoh Corp., Tokyo, Japan, May 31, 1989.
60. G. Thomas, "HREM of Warm Superconductors," College of Engineering Industrial Liaison Trip, Matsushita Electric Co., Osaka, Japan, May 31, 1989.
61. G. Thomas, "Characterization of Electronic Ceramics," College of Engineering Industrial Liaison Trip, Sumitomo Electric, Osaka, Japan, June 1, 1989.
62. G. Thomas, "Characterization of Advanced Materials by Electron Microscopy," University of Lyons, France, June 7, 1989.
63. G. Thomas, "Characterization of Advanced Materials by Electron Microscopy," plenary lecture, 12th ICXOM Conference, Cracow, Poland, Aug. 28-Sept. 1, 1989.
64. G. Thomas, "Characterization of Alloys, Ceramics and Composites of Interest to the Aluminum Industry," Alcoa Technical Center, Alcoa Center, PA, Sept. 11, 1989.
65. G. Thomas, "Characterization of Advanced Materials by Electron Microscopy," Carnegie Mellon University, Pittsburgh, PA, Sept. 12, 1989.
66. G. Thomas, "Atomic Imaging of Inorganic Materials," plenary lecture, 3rd Balkan Congress on Electron Microscopy, Athens, Greece, Sept. 18-23, 1989.
67. G. Thomas, "High Voltage, High Resolution Electron Microscopy," plenary lecture, SIME ATTI Congress, Lecce, Italy, Oct. 2-6, 1989.
68. G. Thomas, "Characterization of Advanced Ceramic and Magnetic Materials," Kawasaki Steel Corp., Chiba, Japan, Nov. 29, 1989.
69. G. Thomas, "Microanalysis of Electronic Ceramics," Mitsubishi Mining and Cement Co., Chichibu, Japan, Dec. 1, 1989.
70. G. Thomas, "Characterization of Advanced Ceramic Materials," Sagami Institute of Science and Technology, Kanagawa, Japan, Dec. 2, 1989.
71. G. Thomas, "Characterization of Advanced Ceramic Materials by Electron Microscopy," First Japan SAMPE Conference, Chiba, Japan, 1989.

[†]Funded by the National Science Foundation.

Solid-State Phase-Transformation Mechanisms*

K.H. Westmacott, Investigator

INTRODUCTION

This research is directed towards obtaining an atomic-level understanding of the structural factors that govern phase changes and phase stability. Transmission electron microscopy techniques, particularly high-voltage and high-resolution microscopy, are employed to characterize phase changes and to infer the atomic rearrangements occurring during a transformation. By studying alloy systems characterized by strains of different signs and magnitudes, the fundamental mechanisms for a broad range of phase transformations are being identified. It has been possible to predict precipitate morphologies (growth directions, habit planes, orientation relationships, substructure, twinning, etc.) from first principles and to relate them to nucleation-and-growth processes. Extension of the principles from simple model alloy systems to more complex materials is now in progress.

1. The Martensitic Transformation in Silicon (Publications 8-10)

P. Pirouz,[†] R. Chaim,[‡] U. Dahmen, and K.H. Westmacott

Ribbons of hexagonal material are produced when silicon is indented in the temperature range 400-650°C. This series of three papers, based on two previous preliminary reports, is a detailed account of an investigation of this phase. In the first paper, the details of the experimental investigation are described. Vickers microindentations were made in float-zone silicon in the temperature range of 400-500°C. The ribbons of hexagonal silicon were then studied by different techniques of transmission electron microscopy (TEM). Conventional microscopy (using strain-contrast, selected-area-diffraction techniques) and high-resolution electron microscopy (HREM) have been employed to investigate the structure of the hexagonal phase. Using the latter technique, the

ribbons are investigated to within a resolution of 0.18 nm, and HREM images are compared with simulated ones. HREM is specifically useful for studying the faulting within the hexagonal phase and the cubic/hexagonal interface. Analytical microscopy using electron-energy-loss spectroscopy (EELS) has been used to show that no oxygen is present in the ribbons within the resolution of this technique. Throughout the paper, it has been attempted to show that the present hexagonal Si is not a thermodynamically stable high-pressure phase, but is related to stress relief when twins interact in silicon. In part II of this series, a mechanism for formation of hexagonal silicon by double twinning is presented through a crystallographic analysis. Finally, in part III, a discussion of the results in the context of martensitic transformations and dislocation mechanisms is given, and other recent reports of this phase in silicon that has undergone different treatments are discussed.

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2. On the Formation of Twinned Precipitates in Al-Ge Alloys (Publication 11)

J. Douin,[†] U. Dahmen, and K.H. Westmacott

High-resolution microscopy has been used systematically to obtain a detailed understanding of the morphology and substructures of Ge needle or lath precipitates in an Al-Ge alloy. We show that the many orientation relationships observed in twinned $\langle 100 \rangle$ and $\langle 110 \rangle$ needles can be related to only three basic lattice correspondences. The feature common to $\langle 100 \rangle$ and $\langle 110 \rangle$ needles is the arrangement of five cozoal twin segments whose relative degree of development determines the cross-section morphology. Some precipitates that displayed apparently irrational orientation relationships (see Figure 2-1) could be related to a rational orientation relationship by multiple twinning (see Figure 2-2). Proposed growth mechanisms based on multiple twinning can account for the formation of all the different observed precipitate morphologies and defect substructures. The central role of twinning and the critical need for vacancies during nucleation are discussed in terms of possible models for nuclei that maximize the number of Ge-Ge bonds through twinning and thus minimize the need for vacancies.

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Figure 2-1. High-resolution transmission electron micrograph of an end-on $\langle 110 \rangle$ Ge needle precipitate in a $\langle 110 \rangle$ Al matrix. The apparently irrational orientation relationships of the twinned segments (4 and 5) are related to a rational orientation relationship by multiple twinning, as shown in Figure 2-2. (XBB 894-3219)

3. Aspects of Faceting in the Study of Precipitate Interfaces (Publication 14)

U. Dahmen, M.J. Witcomb,[†] and K.H. Westmacott

The role of faceting in the formation of interface structures between a precipitate and its matrix is considered and illustrated with TEM observations on a number of

Figure 2-2. Schematic diagram showing how twin segments 4 and 5 in Figure 2-1 are related to the rational orientation of segment 1 by tertiary and quaternary twinning, respectively. The inner polygon represents the projections of low-index planes in the $\langle 011 \rangle$ zone of the Ge, and the outer polygon the Al matrix. The rational orientation relationship of segment 1 is $\{111\} \text{ Ge} \parallel \{110\} \text{ Al}$ and $\langle 110 \rangle \text{ Ge} \parallel \langle 110 \rangle \text{ Al}$. (XBL 894-1477)

different alloy systems. Crystal symmetry and elastic constraints from the solid matrix are shown to be important factors in the development of morphologies and interfacial structures. A typical example of the facets that form on precipitate plates during a low-temperature aging treatment is given in Figure 3-1. Three sets of variants of Θ' precipitates in Al-4% Cu are seen; the two sets of plates parallel to the electron beam show the major facet corresponding to the habit plane, while the third set, imaged normal to the electron beam, illustrates the subsidiary facets.

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4. Work in Progress

Atomic-resolution images have been obtained from monolayer and double-layer Pt-carbide precipitates. In earlier work the precipitates were thoroughly characterized by conventional TEM and the crystal structures of the two metastable phases were determined. Computer-simulated images based on these models are being compared with the experimental images to see if the ARM is capable of discriminating carbon atoms in the structure. Preliminary results are very encouraging and suggest that it will, indeed, be possible to detect and image a single atomic layer of carbon in a matrix of platinum.

Figure 3-1. Conventional TEM dark-field micrograph of faceted Θ' $\{100\}$ precipitate plates in an Al-4% Cu alloy heat treated to promote faceting. (XBB 899-8133)

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. M.J. Witcomb, U. Dahmen, and K.H. Westmacott, "The Coprecipitation of Cr_3P and Cr in Cu," *Ultramicroscopy* **30**, 143 (1989); LBL-24953.
2. U. Dahmen and K.H. Westmacott, "The Use of Heteroepitaxy in the Fabrication of Bicrystals for the Study of Grain Boundary Structure," *Scripta Metall.* **22**, 1673 (1988); LBL-25602.
3. U. Dahmen, C. Hetherington, P. Pirouz, and K.H. Westmacott, "The Formation of Hexagonal Silicon at Twin Intersections," *Scripta Metall.* **23**, 269 (1989); LBL-26233.
4. U. Dahmen, J. Douin, C. Hetherington, and K.H. Westmacott, "High Resolution Electron Microscopy of Interfaces in Topotaxial and Epitaxial Reactions," *MRS Symp. on High Resolution Microscopy of Materials* **139**, 87 (1989); LBL-26545.

Other Publications

5. U. Dahmen and K.H. Westmacott, "Using Crystallographic Symmetry in Diffraction and Contrast Analysis," in *Proc. 47th Annual Meeting EMSA*, San Antonio, TX, G.W. Bailey, Ed., 1989, p. 504; LBL-26920.
6. C. Hetherington, U. Dahmen, P. Pirouz, and K.H. Westmacott, "HREM of Twin Intersections in Silicon," in *Proc. 47th Annual Meeting EMSA*, San Antonio, TX, G.W. Bailey, Ed., 1989, p. 132; LBL-26929.
7. K.H. Westmacott, U. Dahmen, and M.J. Witcomb, "Carbides of Platinum," in *Proc. Symp. on High Temperature and Materials Chemistry*, Berkeley, CA, 1989, p. 11; LBL-27905.

LBL Reports

8. P. Pirouz, R. Chaim, U. Dahmen, and K.H. Westmacott, "The Martensitic Transformation in Silicon: 1. Experimental Observations," *Acta Metall.* (in press); LBL-27071.
9. U. Dahmen, K.H. Westmacott, P. Pirouz, and R. Chaim, "The Martensitic Transformation in Silicon: 2. Crystallographic Analysis," *Acta Metall.* (in press); LBL-27072.
10. P. Pirouz, U. Dahmen, K.H. Westmacott, and R. Chaim, "The Martensitic Transformation in Silicon: 3. Comparison with Other Work," *Acta Metall.* (in press); LBL-27073.
11. J. Douin, U. Dahmen, and K.H. Westmacott, "On the Formation of Twinned Precipitates in Al-Ge Alloys," submitted to *Philos. Mag.*; LBL-27258.
12. K.H. Westmacott and U. Dahmen, "High Voltage/High Resolution Studies of Metal and Semiconductor Interfaces," in *Proc. Intl. Symp. on EM in Plasticity*, Holzgau, German Democratic Republic, Oct. 8-13, 1989 (in press); LBL-26274.

13. U. Dahmen and K.H. Westmacott, "Control of Interfaces for TEM Analysis," submitted to *J. Electron. Microsc. Tech.*; LBL-27259.
14. U. Dahmen, M.J. Witcomb, and K.H. Westmacott, "Aspects of Faceting in the Study of Precipitate Interfaces," submitted to *J. de Physique Colloque*; LBL-27834.
15. J. Douin, U. Dahmen, and K.H. Westmacott, "A High Resolution Study of Twinned Precipitates in Al-Ge Alloys," submitted to *J. de Physique Colloque*; LBL-28389.
16. U. Dahmen and K.H. Westmacott, "Problems of Enclosed Crystal Interfaces," in *Proc. Indo-U.S. Workshop on Interfaces: Structure and Properties*, Bangalore, India, Dec. 1989 (in press); LBL-28388.
17. K.H. Westmacott and U. Dahmen, "Studies of Faceting by High Voltage/High Resolution Microscopy," in *Proc. Indo-U.S. Workshop on Interfaces: Structure and Properties*, Bangalore, India, Dec. 1989 (in press); LBL-28389.

Invited Talks

18. U. Dahmen and K.H. Westmacott, "High Resolution Imaging of Near-Sigma $\langle 110 \rangle$ Boundaries in Aluminum," *EMSA*, Durban, South Africa, Dec. 1988.
19. K.H. Westmacott and U. Dahmen, "Fundamental Studies of Grain Boundary Structure and Properties in ICB Aluminum," *ISIAT'89 Conference*, Tokyo, Japan, June 5-7, 1989.
20. K.H. Westmacott, "Structure and Properties of Al Bicrystals," *Max Planck Institute*, Stuttgart, Federal Republic of Germany, Oct. 4, 1989.
21. K.H. Westmacott, "The Role of Twinning in Precipitate Formation in Al-Ge," *Halle University*, Halle, Federal Republic of Germany, Oct. 6, 1989.
22. K.H. Westmacott and U. Dahmen, "High Voltage/High Resolution Studies of Metal and Semiconductor Interfaces," *International Symposium of EM in Plasticity*, Holzgau, German Democratic Republic, Oct. 8-13, 1989.
23. K.H. Westmacott and U. Dahmen, "Hot Stage Studies of Homophase and Heterophase Interfaces," *Indo-U.S. Workshop on Interfaces: Structure and Properties*, Bangalore, India, Nov. 30-Dec. 3, 1989.
24. U. Dahmen and K.H. Westmacott, "Problems of Enclosed Crystal Interfaces," *Indo-U.S. Workshop on Interfaces: Structure and Properties*, Bangalore, India, Nov. 30-Dec. 3, 1989.
25. U. Dahmen, M. Witcomb, and K.H. Westmacott, "Morphology and Interface Structure of Lath-Shaped Precipitates in Cu-Cr Alloys," *Annual TMS Meeting*, Las Vegas, NV, Feb. 1989.
26. U. Dahmen, "Crystal Mirrors as Markers in Microscopy of Materials," *NCSEM*, San Francisco, Mar. 1989.
27. U. Dahmen, "Electron Microscopy Characterization of Defects and Precipitates," *Summer School on Electron Microscopy*, Stockholm, Sweden, Aug. 20-25, 1989.
28. U. Dahmen, M.J. Witcomb, and K.H. Westmacott, "Aspects of Faceting in the Study of Precipitate Interfaces," *International Congress on Intergranular and Interphase Boundaries in Materials*, Paris, Sept. 4-8, 1989.

29. U. Dahmen, "Crystallographic Aspects of Ledge Growth," International Symposium on Ledges, TMS/AIME Annual Meeting, Indianapolis, IN, Oct. 2-6, 1989; LBL-27195abs.
30. U. Dahmen, "TEM Studies of Interfaces and Phase Transformations," Exxon Research Laboratories, Annandale, NJ, Oct. 6, 1989.
31. U. Dahmen, "Aspects of Symmetry in Phase Transformations," Department of Materials Science and Engineering, University of California, Berkeley, Oct. 12, 1989.
32. U. Dahmen, M.J. Witcomb, and K.H. Westmacott, "Carbides of Platinum," Brewer Symposium on High Temperature and Materials Chemistry, LBL, Oct. 24-25, 1989.

National Center for Electron Microscopy*

Gareth Thomas, Ronald Gronsky, and Kenneth H. Westmacott, Investigators

INTRODUCTION

The National Center for Electron Microscopy (NCEM) provides advanced facilities for electron-optical characterization of materials. Its resident staff operate, maintain, design, and develop equipment and software, making it available to all Center users, and in addition conduct their own forefront research on problems in the materials sciences.

Central to NCEM are two unique high-voltage electron microscopes, a 1.5-MeV machine (the High-Voltage Electron Microscope, or HVEM), which is the most powerful in the U.S., and a 1-MeV machine (the Atomic Resolution Microscope, or ARM), which offers the best resolution in the world (better than 1.6 Å). These instruments are backed by "feeder" microscopes (for specimen screening, preliminary experiments, and complementary microchemical analysis), by specimen-preparation facilities, and by image processing and analysis facilities, all within the same building and exclusively dedicated to electron microscopy.

The 200-keV analytical microscope (AEM) is fully utilized in support of Center research. Current projects on the instrument include standard analyses as well as the development and refinement of new techniques (e.g., electron-energy-loss spectroscopy and convergent-beam electron diffraction) and software for quantification. The NCEM computer system is designed to assist interpretation of electron microscope images in three ways: (1) real-time enhancement of live video-rate TV images from the electron microscopes under control of the microscope operator; (2) interactive *a posteriori* processing of stored experimental images at a work station hosted by the computer; and (3) matching experimental images to ones simulated from a proposed model structure at a work station controlled by the host computer, in order to confirm (or reject) the suitability of the model.

*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Operations (2) and (3) are running and available for users at a two-station Gould IP8500 image processor controlled by the microVAX. For implementation of operation (3), a second microVAX is available to control sets of DataCube modules that will digitize a video image in real time, store it in memory, average it over a (selected) time interval to improve the signal-to-noise ratio, and display the enhanced image on the microscope operator's monitor. A small array processor (MCS ZIP3232) provides background correction and the capability to present the operator with the diffractogram of the image.

Guidance for NCEM is provided by a steering committee, chaired by J.J. Hren (North Carolina State University). Its present members are C.W. Allen (Argonne National Laboratory), D.J. Smith (Arizona State University), U. Dahmen (LBL), T. Hayes (LBL), D.G. Howitt (University of California, Davis), F. Ponce (Xerox Palo Alto Research Center), L.E. Thomas (Battelle Pacific Northwest Laboratory), M.M.J. Treacy (Exxon R&D), and the investigators on this project. Meetings are held yearly.

Research projects at the Center cover a wide spectrum, including phase-transformation studies in metals, ceramics, and minerals; and high- T_c superconductors, semiconductor devices, catalyst and amorphous-metal investigations, as well as biological medical-science applications.

Ongoing research projects at NCEM are listed in Table 1-1.

Some examples of recent research at the Center are listed below.

1. High-Resolution Electron Microscopy (HREM) of Interfaces in Topotaxial and Epitaxial Reactions (Publication 37)

U. Dahmen, J. Douin, C.J.D. Hetherington, and K.H. Westmacott

In the study of interfaces, HREM is most useful when the interface is viewed edge-on while both crystals are accurately aligned along low-index zone axes. The formation of such interfaces by epitaxy or topotaxy is the natural means of obtaining structures that can be usefully analyzed by HREM. Furthermore, there is intense interest in understanding the atomic structure of such interfaces in a variety of technologically important materials. This contribution addresses such structures produced by thermal decomposition, precipitation reactions, and ionized-cluster-beam deposition, and reports on the structural investigation of symmetrical and asymmetrical grain boundaries, precipitate/matrix interfaces, internal defect structure of precipitates, and nanocrystalline composites.

Table 1-1
NCEM Research Proposals (active during 1989)

Principal Investigator	Affiliation	Title
HVEM		
J. Bastacky	LBL/UC Berkeley	The phagocytic process involved in uptake of coal combustion particulates (fly ash) by pulmonary macrophage cells
T. Cass	Hewlett-Packard	Defect structures in semiconductor devices
J. Cornie	MIT	Tailoring and modeling interfaces in metal-matrix composites
U. Dahmen	LBL	Characterization of nanocrystals by TEM
K. Dante	UC Berkeley	Alteration of pyrite to chalcocite
J. Dash	Portland State University	Phase transformation induced by high pressures and temperatures in a ballistic compressor
D. deFontaine	LBL/UC Berkeley	<i>In situ</i> observation of the Devil's Staircase in the long-period superstructures of binary alloys
J. De Natale	Rockwell International	<i>In situ</i> studies on the mechanisms of crystalline transformations in thin film
J. Evans	LBL/UC Berkeley	Thermal oxidation of InP Dynamic transmission electron microscopy
R. Fisher	LBL/IBM	Microstructure investigations of ceramic model interface
D. Frear	Sandia National Laboratory	Microstructural study of Al thin film Microstructure of solder interconnections in electronic packaging polymers
S. Frisia-Bruni	LBL/U. Milan	Microstructural investigation into the diagenetic history of Haupt dolomite of the Southern Alps

Table 1-1 (continued)

Principal Investigator	Affiliation	Title
W. Glassley	LBL/LLNL	Investigation of the alpha/beta cristobalite transition in the presence of a vapor phase
H. Green II	UC Davis	The olivine to spinel transformation in Mg_2GeO_4
R. Gronsky	LBL/UC Berkeley	<i>In situ</i> oxidation study of the Y/Ba/Cu/O superconductors
J. Heuer	Rockwell International	Materials study of mixed composition thin films
J. Howe	Carnegie-Mellon	<i>In situ</i> studies of precipitate growth by a terrace-ledge-kink mechanism
D. Howitt	UC Davis	Structural study of thin-film ceramics
V. Jayaram	UC Santa Barbara	Microstructural study of rapidly solidified powders
M. Kassner	LLNL	Delayed failure of Ag-aided diffusion bonds by microvoid coalescence
E. Kvam	LBL	Dislocation dynamics in strained epitaxial Ge-Si alloys on (001) silicon
Z. Liliental-Weber	LBL	Study of the kinetics of Au crystallite formation on the periphery of Au Schottky contacts
M. Madden	Intel	Analysis of single bit failures in VSLICs
A. Meike, C. Rüschler	LBL/U. Hanover, FRG	Elementary steps of biotite buffer reactions
A. Meike	LBL	Characterization of stress-induced defects in minerals in relation to enhanced aqueous dissolution
J. Morris, Jr.	LBL/UC Berkeley	Dislocation substructures and work-hardening in bcc polycrystalline metals
D. Noble	Stanford	Misfit dislocation in SiGe/Si heterostructures

Table 1-1 (continued)

Principal Investigator	Affiliation	Title
L. Rehn	Argonne National Laboratory	Comparison of electron and ion-irradiation-induced grain growth in gold films
R. Ritchie	LBL/UC Berkeley	Dynamic studies of deformation and failure in SiC-aluminum metal-matrix composites
M. Robinson	U. Capetown, South Africa	<i>In situ</i> straining of Al and Al-Mg alloys within the serrated flow regime
M. Ruhle	UC Santa Barbara	Bridging mechanisms of toughening in whisker-reinforced ceramics
A. Searcy	LBL/UC Berkeley	TEM studies of decomposition reactions
G. Shiflet	U. Virginia	HVEM of pearlite in a Fe-C-Mn alloy
L. Tanner	LLNL	Study of metastable phase formation in Cu-Zr and Al-Ni
M. Taylor	UC Davis	Hydration of Portland cement in environmental cell
Gareth Thomas	LBL/UC Berkeley	<i>In situ</i> studies of dislocation glide/climb in Al-Li A systematic study of Cu-Ni thin films for magnetic recording media
Gareth Thomas, A. Berkowitz	LBL/UC San Diego	The transformation of $\alpha\text{Fe}_2\text{O}_3 \rightarrow \text{red} \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{oxid} \rightarrow \gamma\text{Fe}_2\text{O}_3$
George Thomas	Sandia National Laboratory	<i>In situ</i> oxidation studies on stainless steel Gases in metals
P. Vasconcelos	UC Berkeley	Microstructures in natural gold: influence of high Hg and Pd content

Table 1-1 (continued)

Principal Investigator	Affiliation	Title
R. Wenk	UC Berkeley	Phase transformation in silica minerals Deformation mechanisms in dolomite polycrystals as a function of orientation Influence of defects on a-b quartz transformation and Dauphine twinning
K. Westmacott	LBL	Dynamic hot-stage studies of precipitate development in interstitial and substitutional alloys TEM study of the annealing and deformation of aluminum bicrystals
C. Wong	GM	The effects of oxidation-reduction treatments on the morphology of supported rhodium catalysts
ARM		
P. Alivisatos	UC Berkeley	TEM studies of semiconductor clusters
S. Chumbley	NASA Ames	Analysis of deformed superconductors
J. Cornie	MIT	Tailoring and modeling interfaces in metal matrix composites
U. Dahmen	LBL	Characterization of nanocrystals by HREM HREM study of ionized-cluster-beam (ICB) deposited metal clusters
T. Epicier	LBL/INSA, GEMPPM, France	Atomic resolution microscopy of light atoms in some ceramic compounds HREM study of alumina-based ceramics
J. Goral	SERI	High-resolution structural study of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ Ordering in GaInP Defect generation and propagation in MBE-grown GaAs/GaInAs

Table 1-1 (continued)

Principal Investigator	Affiliation	Title
R. Gronsky	LBL/UC Berkeley	Atomic mechanisms of precipitate plate growth Quasicrystals Defects in oxide superconductors Defect reduction in ISE SOI material HREM of thin-film superconductors: epitaxy and metal contact interfaces
R. Herring	Martin-Marrietta	HREM of T ₁ -type phases in Al alloys
J. Howe	Carnegie-Mellon U.	Atomic resolution studies of shearable coherent precipitates in Al-Li alloys Atomic resolution microscopy of interfaces in intermetallic-matrix composites Atomic resolution studies of {225} martensite-austenite interfaces
A. Jankowski	LLNL	Interfacial structure of short-period Au/Ni multilayers
W. Kriven	U. Illinois	TEM characterization of modulated structures in CaO-Dy ₂ O ₃ solid solutions
E. Kvam	LBL	Systematic study of grain-boundary structures in fcc[001] tilt boundaries
J. Laval	CNRS, Paris	Atomic structure of internal interfaces in covalent materials
Z. Liliental-Weber	LBL	The structure of metal contacts to GaAs
J. Mayer	UC Santa Barbara	HREM structural studies of interfaces between high-temperature superconductors and substrates
M. Mills	Sandia, Livermore	Core structure of screw super dislocations in Ni ₃ Al

Table 1-1 (continued)

Principal Investigator	Affiliation	Title
J. Morris	LBL/UC Berkeley	Analysis of fine microstructures in Al-Sc-(RE)
G. Olson	MIT	Fine structure of martensitic interfaces
F. Ponce	LBL/Xerox	Structure of early stages of growth in GaAs/Si epitaxy
M. Ruhle	UC Santa Barbara	HREM study of Pd/Al ₂ O ₃ interfaces with modulated structures
A. Schwartzman	Stanford	Core structure of Lomer dislocations at the CdTe/GaAs and ZnTe/GaAs interfaces
G. Shiflet	U. Virginia	HREM growth ledges on T1 (Al ₂ CuLi) plates
		HR studies of interfacial pearlitic structures in a Fe-C-Mn alloy
R. Sinclair	Stanford	Structure of twin interfaces in TiNi
M. Suenaga	Brookhaven National Laboratory	Twin boundaries in YBa ₂ Cu ₃ O ₇
L. Tanner	LLNL	HRTEM studies of pretransformation microstructures in metallic alloys
		Study of metastable formation in Cu-Zr and Al-Ni
Gareth Thomas	LBL/UC Berkeley	HREM on glasses
		Structure of PFZ in Al-Li alloys
		Atomic imaging of structure and defects in high T _c -superconductors
		Structure and interfaces in NiO/CoO
		Formation mechanism of (Al ₃ Li)
George Thomas	Sandia, Livermore	Structure of high-T _c superconductors
		Structure of grain boundaries in metals

Table 1-1 (continued)

Principal Investigator	Affiliation	Title
H. Wenk	UC Berkeley	Superstructure identification in carbonate minerals
		Electron crystallography of minerals
K. Westmacott	LBL	Studies of precipitate morphologies and interfaces
		TEM study of the deformation of aluminum bicrystals
AEM		
K. Krishnan	LBL	Iron L _{3,2} near-edge fine-structure studies
		Characterization of low-pressure diamond films
		Applications and development of channelling enhanced microanalysis
K. Krishnan, N. Cho	LBL	Characterization of diamond-like carbon
K. Krishnan, V. Yachandra, M. Klein	LBL	White lines in manganese oxides and complexes
K. Krishnan, C. Echer	LBL	Experimental determination of energy-loss cross sections for low-atomic-number elements
C. Ortiz, K. Krishnan	LBL/IBM San Jose	Microstructural characterization of Fe-oxide magnetic recording media
C. Ortiz, J. Adams, C. Echer	LBL/IBM San Jose	Microstructural characterization of laser-modified Br-Te-Se thin films
R. Shen, K. Krishnan, N. Bartlett	LBL/UC Berkeley	EELS analysis of B-C-N chemically vapor-deposited crystallites
		Characterization of new graphite-like materials (C _x B _y N ₂) by electron-energy-loss spectroscopy
R. Fernandes, K. Krishnan, C. Echer	LBL/U. Zimbabwe	AEM characterization of Zimbabwe chromite deposits

Table 1-1 (continued)

Principal Investigator	Affiliation	Title
S. Patankar	NM Inst. Mining and Tech.	Microstructural characterization of alumina/glass interfaces
D. Blake, C. Echer	LBL/NASA Ames	Characterization of carbonaceous phases contained in meteorites and interplanetary dust particles
		Carbon characterization of Murchison meteorite
Z. Liliental-Weber, J. Washburn, R. Gronsky	LBL	Ohmic and Schottky Au contacts on GaAs
Z. Liliental-Weber, T. George, E. Weber	LBL/UC Berkeley	Microstructural characterization of Zr oxides and nitride interfaces with GaAs
N. Merk, L. Tanner	LBL/LLNL	Solid-state amorphous reactions during mechanical alloying of Ni/Ta powders contaminated with WC crystals
		Characterization of Ni/Al and Cu/Zr solid-state phase transformations
N. Merk, G. Thomas	LBL/UC Berkeley	Characterization of mullite whiskers
		Characterization of metal/ceramic interfaces
N. Kijima, R. Gronsky	LBL	Microstructural characterization of Sb-Pb-Bi-Sr-Ca-Cu-Co superconductors
R. Crook, C. Echer, R. Fisher	LBL/Rockwell International	Microstructural characterization of titanium-aluminum alloy/alumina interface region at 1000°C
N. Benson, C. Echer, K. Krishnan	LBL/Cal State Hayward	Characterization to determine the presence and valence of reduced selenium in bacteria
S. Menon, P. Huang, K. Krishnan, D. deFontaine	LBL/UC Berkeley	Characterization of short-range order and long-period superstructures in Cu-Pd alloys
K. Liu, Gareth Thomas	LBL/UC Berkeley	Reaction sintering: kaolinite → mullite

Table 1-1 (continued)

Principal Investigator	Affiliation	Title
C. Kochler, Gareth Thomas	LBL/UC Berkeley	Microstructural evaluation to improve high-temperature properties of Y-SiAlON
C. Koestler, C. Echer, Gareth Thomas	LBL/UC Berkeley	Microstructural characterization of Fe-Co-Nd-B melt-spun magnets containing various Co contents
K. Lin, Gareth Thomas	LBL/UC Berkeley	Characterization of Co-Ni-Cr magnetic thin films
C. Leroux, Gareth Thomas	LBL/UC Berkeley	Characterization of antiferromagnetic NiO/CoO films
T. Li, Gareth Thomas	LBL/UC Berkeley	Characterization of Co-Ni-Cr and Co-Ni-Ta recording thin films
M. Cinibulk, Gareth Thomas	LBL/UC Berkeley	Characterization of silicon nitride/SiAlON composites
D. Callahan, Gareth Thomas	LBL/UC Berkeley	Characterization of oxygen in aluminum nitride ceramics
V. Radmilovic, Gareth Thomas	LBL/UC Berkeley	Characterization of metal-matrix composites—aluminum alloys
		Interfacial characterization of silicon nitride and aluminum alloys
		Characterization of copper oxide in high-purity copper
V. Radmilovic, F. Chen, C. Echer, T. Devine	LBL/UC Berkeley	Characterization of type 308 and 304 stainless steel weldments that showed intergranular stress-corrosion cracking in H.A.Z.
C. Willis, T. Devine	LBL/UC Berkeley	Characterization of elemental partitioning on phase boundaries in 308 stainless steel
C. Kumai, T. Devine	LBL/UC Berkeley	Copper concentration variations in Al-Li-Cu-Mg powder alloys
A. Motta	LBL/UC Berkeley	Characterization of proton-irradiated Zircaloy

Table 1-1 (continued)

Principal Investigator	Affiliation	Title
T. Epicier, C. Echer,	LBL/INSA, France	Characterization of dislocations in W_2C and Al_2TiO_5 after HVEM irradiation
A. Goldstein, P. Alivisatos	UC Berkeley	Elevated-temperature characterization of CdS microcrystallites
J. Goral	SERI	Characterization of copper-containing impurity phases in $CuInSe_2$ polycrystalline thin films
S. Bruni, R. Wenk	U. Milan/UC Berkeley	Microstructural investigation of Southern Alps dolomites
R. Wenk, M. Medrana, M. Hu	UC Berkeley	Investigation of apparent differences between Sillimanite and Fibrolite
K. Dante, M. Hu, R. Wenk	UC Berkeley	Characterization of copper-containing pyrite
R. Wenk, M. Hu, P. Vasconcelos	UC Berkeley	Characterization of Amazonian gold nuggets
D. Sinitsyna, R. Wenk	UC Berkeley	Characterization of perovskites and dolomites
A. Meike	LBL/UC Santa Cruz	Microchemical analysis of trace pigment observed on an Egyptian carved limestone head (ca. 2400 B.C.)
W. Hirt, R. Wenk	LBL/UC Berkeley	EDX and EELS characterization of pyroxene and dolomite
J. Douin, U. Dahmen, K. Westmacott	LBL	Microstructural characterization of precipitates in aluminum-1% germanium alloys
M. Witcomb, U. Dahmen	LBL/U. Witwatersrand, South Africa	Microstructural characterization of chromium-rich precipitates in Cu-Cr alloys
A. Fox	Naval Postgraduate School, Monterey	Dislocation characterization of solid-state bonding of copper to glass

Table 1-1 (continued)

Principal Investigator	Affiliation	Title
Computer Projects		
R. Rai, M. O'Keefe	LBL/UC Berkeley	Processing of images of phases of yttrium disilicate Simulation of phases in $Y_2Si_2O_7$
M. Sattler, M. O'Keefe	LBL/UC Berkeley	Processing of images of multilayer structures formed from amorphous materials
R. Kilaas, K. Krishnan, R. Rai	LBL/UC Berkeley	Image simulation and processing of 32HR.AIN/Al ₂ O ₃ images
J. Y. Laval, R. Kilaas	LBL/CNRS, Paris	Silicon nitride and interface simulation
M. Sattler, M. O'Keefe	LBL/LLNL	Simulation of interfaces in amorphous materials
N. Schryvers, R. Kilaas	LBL/LLNL	Simulation of "tweed" image of NiAl
U. Dahmen, M. O'Keefe	LBL/UC Berkeley	Simulation of metastable phases in zirconia
C. Jou, R. Kilaas	LBL/UC Berkeley	Oxygen vacancies in YBa ₂ Cu ₃ O _{7-d}
N. Merk	LBL/LLNL	Diffraction pattern calculation in CuZr-NiAl
M. Stampfer	LBL	Quantification in energy-loss spectroscopy
C. Hetherington	LBL	ARM characterization (CTFs, on-line ODM) Al grain-boundary processing (SEMPER)
C. Hetherington, M. O'Keefe, R. Kilaas, A. Fox	LBL/U. Wolverhampton	Wedge crystal study of experimental image vs calculated image
C. Hetherington, U. Dahmen	LBL	Hexagonal silicon and hexagonal/cubic interface
J. Douin, U. Dahmen	LBL	Interface simulation in Al/Si-Al/Ge

Table 1-1 (continued)

Principal Investigator	Affiliation	Title
T. Epicier, R. Kilaas, K. Krishnan	LBL/INSA, Lyon, France	Studies of mullite; studies of C_6O cluster
M. O'Keefe, R. Kilaas	LBL	Simulation of Al grain boundaries
R. Ramesh, C. Hetherington, M. O'Keefe	LBL/UC Berkeley	Simulations of modified BSCCO high- T_c superconductors
M. O'Keefe, M. Sattler	LBL/LLNL	Simulation of multilayer structures
J. Wong, M. O'Keefe	LBL/LLNL	Simulation of substituted high- T_c superconductors
M. O'Keefe, D. Blake	LBL/NASA Ames	Processing of interstellar diamond images
A. Motta, J. Turner	LBL/UC Berkeley	Computer-intensity analysis of diffraction patterns from Zircaloy
U. Dahmen, J. Turner	LBL	Diffraction-pattern profiles of MgOH
		Image processing of ICB aluminum grain boundaries to determine periodicity
		Image processing of models for the determination of crystal misorientations represented in the optical diffractograms
R. Ramesh, J. Turner	LBL/UC Berkeley	HREM image processing of the $Bi_2Sn_2Ca_2Cu_3O_4$ superconductor
T. Epicier, J. Turner	LBL/INSA, Lyon, France	Fourier filtering of HREM images of mullite
N. Thangaraj, J. Turner, M. O'Keefe	LBL	Processing of ICBD Ag particles
J. Ulan, M. O'Keefe	LBL/UC Berkeley	Simulation of Zeolite images
J. Ulan, J. Turner, M. O'Keefe	LBL/UC Berkeley	Processing of Zeolite images
R. Ramesh, R. Kilaas	LBL/Bell Communications	Studies of copper vacancies in high- T_c superconductors

Table 1-1 (continued)

Principal Investigator	Affiliation	Title
N. Merk, R. Kilaas	LBL/UC Berkeley	Simulation studies of displacement waves and concentration waves in NiAl
U. Dahmen, R. Kilaas	LBL	Development of software algorithms for the construction of general crystal interfaces
U. Dahmen, R. Kilaas	LBL	Computer models for cluster formation under vapor deposition
M. Hu, R. Wenk, M. O'Keefe	LBL/UC Berkeley	Simulation studies of stauralite

2. Atomic Structure of a $\Sigma 99$ Grain Boundary in Aluminum: A Comparison Between Atomic-Resolution Observation, Pair Potential, and Embedded-Atom Simulations (Publication 65)

U. Dahmen, C.J.D. Hetherington, M.A. O'Keefe, K.H. Westmacott, M.J. Mills,[†] M.S. Daw,[‡] and V. Vitek[‡]

An atomic-resolution image of a symmetrical $\Sigma 99$ {557} $\langle 110 \rangle$ tilt boundary in aluminum is compared with images simulated from models based on atomistic calculations by the pair-potential method (PPM) and the embedded-atom method (EAM). Because the relaxed boundary structures predicted by both types of calculation are strongly dependent on the initial configuration used, feedback from experimental images is important in the search for a minimum energy structure. The two methods for atomistic modeling give almost identical structures (see Figure 2-1), and image simulations based on such structures closely match the experimental results.

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3. Structural and Electrical Characterization of InAs Grown on GaAs Substrates by Molecular-Beam Epitaxy (Publication 24)

P. Sheldon,[†] M.M. Al-Jassim,[†] K.M. Jones,[†] J.P. Goral,[†] and B.G. Yacobi[‡]

Epitaxial InAs:Sn is grown on semi-insulating GaAs substrates by molecular-beam epitaxy. The large lattice mismatch between these materials ($\sim 7.1\%$) generates a high density of threading dislocations that propagate into the epitaxial film. Both plan-view and cross-sectional transmission electron microscopy techniques are used to investigate the generation and propagation of these dislocations. For films that exceed the critical thickness, the threading dislocation density is inversely proportional to the epilayer thickness. Epitaxial layers incorporating growth interrupts have lower overall defect densities, yet maintain defect reduction profiles similar to those observed in layers grown without the growth interrupt. Room-temperature mobilities for InAs:Sn epitaxial layers varied from 11,200 to 22,100 $\text{cm}^2/\text{V}\cdot\text{sec}$ for epilayer thicknesses of 0.4 to 4.4 μm , respectively. The thickness dependence on the mobility is attributed to a multiplicity of factors,

Figure 2-1. Comparison of the lowest energy structures calculated by the two computational models, EAM (a) and PPM (b). The displacement map (c) compares the two simulated structures by arrows pointing from the EAM to the PPM. The longest arrow corresponds to a relative atomic displacement of about 0.05 nm. [XBB 890-10225 (a, b); XBL 8911-4265 (c)]

including surface scattering, interfacial strain, surface accumulation, and the high interfacial dislocation density.

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4. High-Resolution Electron Microscopy of Grain Boundaries in Nanophase Palladium (Publication 58)

G.J. Thomas,[†] R.W. Siegel,[‡] and J.A. Eastman[‡]

Using high-resolution electron microscopy, consolidated nanophase palladium samples were examined following electrolytic thinning after a hydriding-dehydriding cycle at 310 K. Due to the small size and random orientations of the individual grains, a large number of grain boundaries were available for examination. Some of these yielded adequate imaging conditions to allow observation of the lattice structure in the grain-boundary regions. Image simulations were performed to determine the sensitivity of the technique to lattice disorder. The results of these studies suggest that grain-boundary structures in nanophase palladium are similar to those in conventional coarse-grained polycrystals.

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5. Atomic Imaging of 3:2 Mullite (Publication 73)

T. Epicier,[†] M.A. O'Keefe, and G. Thomas

The crystallographic structure of $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ mullite has been studied by means of high-resolution electron microscopy. The best conditions for atomic imaging of this compound are discussed relative to the ARM. Multibeam images in the [001] direction have been produced at 0.19-nm resolution, allowing the cation sublattice to be imaged directly, with a firm transfer of information on the oxygen sublattice. Under optimal conditions of defocus setting and thickness, typical contrasts have been detected and consistently interpreted in terms of the presence of oxygen vacancies along the defective atomic columns (see Figure 5-1). These observations conclusively prove that the vacancies are not ordered, showing that previous published observations were made under faulty high-resolution imaging conditions.

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6. A High-Resolution Transmission Electron Microscopy Study of a SiC-Coated Graphite Fiber/Aluminum Composite (Publication 13)

Q. Li, J. Megusar, L.J. Masur, and J.A. Cornie[†]

A SiC-coated graphite fiber/aluminum composite was processed by plasma-enhanced chemical vapor deposition (PECVD) of silicon carbide followed by aluminum pressure infiltration. A high-resolution transmission electron microscopy study of this composite was carried out, with emphasis on a detailed characterization of the interface structures. Pitch-55 graphite fiber structure was analyzed in both the core and skin regions, and it resembles that of turbostratic graphite. The SiC coating deposited by the PECVD technique was fully amorphous. The graphite fiber/SiC interface was characterized as sharp. Pressure infiltration of aluminum into fibers of low initial temperature (621 K) almost completely suppressed formation of a reaction zone between the aluminum and SiC. A mismatch in the coefficient of thermal expansion between the components of this composite leads to dislocation generation in the aluminum matrix. These observations allowed for a detailed evaluation of the processing techniques used, and structural details of the interfacial regions will serve at the same time as a basis for modeling interface properties.

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7. The Effect of an Aluminum Heat-Sink Layer on the Laser-Induced Amorphization of $\text{SiO}_x/\text{TeGeSn}/\text{SiO}_x$ Phase-Change Recording Films (Publication 33)

M.R. Libera[†] and M. Chen[†]

Phase-change erasable optical storage is based on the ability to switch a micron-sized region of a thin film between the crystalline and amorphous states using a diffraction-limited laser as a heat source. A bit of information can be represented as an amorphous spot on a crystalline background, and the two states can be optically identified by their different reflectivities. In a typical multilayer thin-film structure, the active (storage) layer is sandwiched between one or more dielectric layers. The dielectric layers provide physical containment and act as a heat sink. A viable phase-change medium must be able to quench to the glassy phase after melting, and this requires proper tailoring of the thermal properties of the multilayer

Figure 5-1. HREM analysis of a thin uniform crystal edge in K-mullite. Top line: low-magnification micrograph taken at Scherzer defocus (~ 50 nm). Details A and B are examined in the second and fourth lines, respectively. Arrows indicate defects similar to the one studied in the micrographs on the fourth line. Second line: through-focus series from detail A above (from left to right, $\Delta f = -50$ nm, -87.5 nm, -97.5 nm, and -117.5 nm; the thickness used in the superimposed calculated image is 1.4 nm, but identical contrasts are obtained within ± 0.5 nm). Third line: corresponding calculated images for a hypothetical structure where oxygen atoms are missing (without any atomic displacements); note the disagreement with experimental images on the second line. Fourth line: enlargement of detail B (from the top line) for three defoci (-50 nm, -87.5 nm, and -97.5 nm); arrows in the first micrograph indicate a distortion of triplets of dark dots. Bottom line: calculated images matching the previous experimental micrographs. These correspond to a 0.9-nm thin crystal with two vacancies along the central O_3 -type oxygen column, according to the model shown on the third line. [XBB 892-769 (top three lines); XBB 892-767 (bottom two lines)]

film. The present research studies one particular multilayer structure and shows the effect of an additional aluminum layer on the glass-forming ability.

A trilayer structure of 1500-Å SiO_x /750-Å TeGeSn /1500-Å SiO_x was deposited on a re-grooved polycarbonate disk by electron-beam evaporation (SiO_2) and thermal co-evaporation (Te, Ge, Sn) near the stoichiometric composition (3) at a pressure of 5×10^{-7} torr. After shielding half of the disk with a semicircular mask, an additional 500 Å of aluminum was evaporated onto the unshielded half. The disk was then subjected to a variety of laser exposures using a dynamic recording tester. This instrument focuses a krypton ion laser through the substrate to an 0.8- μm spot on the active layer, and both the laser focus and its position on the disk are accurately controlled by a servo system. The TeGeSn layer was amorphous when deposited, as a 1-mm band was crystallized by traversing the disk with low-power laser irradiation while spinning at a linear velocity of 4.85 m/sec. Individual tracks in this band-crystallized region were then subjected to 100 nsec laser pulses at 1- μsec intervals for one disk revolution. Adjacent tracks were systematically irradiated with pulses ranging from 25 to 60 mW incident power. After characterizing the recording properties of the disk, TEM specimens were prepared by gluing 100-mesh grids to the thin-film side of the disk (M-bond 610 epoxy) and then dissolving the polycarbonate with methylene dichloride. The specimens were examined in plan view at 1.5 MeV using a Kratos EM1500 TEM.

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8. Short-Range Order in Electron-Irradiated Cu-Pd: Fluctuations in a Nonequilibrium Steady State (Publication 30)

J. Kulik,[†] D. Gratias,[‡] and D. de Fontaine

Electron-diffraction results are presented on specimens of Cu-Pd alloys under irradiation with 1.5-MeV electrons at temperatures from 200 to 400 K. The irradiation induces atomic mobility through the production of point defects but maintains the system in a disordered state despite a long-range-ordered phase being the equilibrium state. The presence of short-range order (SRO) is detected in electron-

diffraction data. SRO in Cu-Pd is characterized by peaks of intensity that flank the 100 and equivalent positions in the Brillouin zone, removed from those positions by a distance q_m . The quantity q varies with Pd content and also with the temperature at which the system is irradiated. An analogy is drawn with an equilibrium statistical model.

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9. *In situ* Deformation of Micas: A High-Voltage Electron Microscope Study (Publication 17)

A. Meike

Muscovite (2M₁) and biotite (1M) were sheared *in situ* at room temperature in a 1500-kV transmission electron microscope. The resultant activation of dislocations represents the first success of such an experiment in a rock-forming mineral. Only basal slip was activated in either mica, but the dislocations could be distinguished on micromechanical grounds that may be related to a macroscopic difference in ductility. Invariably, dislocations in the muscovite specimens activated with greater difficulty, despite the greater abundance of precipitates in the biotite specimens. Muscovite basal dislocations were long and roughly linear, oriented along [100] or [110]. They activated in short steps that advanced parallel to the dislocation line, a manner typical of screw dislocations. In contrast, biotite basal dislocations were curvilinear and advanced perpendicular to the dislocation line in bowed segments, characteristic of edge dislocations. The division of dislocation lines, often separated by areas of either reversed contrast or moiré fringes, was interpreted as dislocation dissociation. Dissociation appeared to facilitate obstacle circumvention in biotite. The proposed explanation for the micromechanical differences is based on the distribution of Peierls potential energy in the basal glide plane and other energy-minimization arguments. The agreement between the proposed model and observation suggests that the micromechanical difference is structurally determined by the octahedral layer. The proposed Peierls stress control of dislocation activity could be evaluated from natural evidence, based on an expected inverse relationship between the magnitude of the micromechanical differences and temperature.

10. Icosahedral Phase Formation in Rapidly Quenched Aluminum-Ruthenium Alloys (Publication 1)

S.M. Anlage,[†] B. Fultz,[‡] and K.M. Krishnan

Systematic rapid quenching experiments on the icosahedral phase-forming system $\text{Al}_{1-x}\text{Ru}_x$ were performed for $x < 20$ at%. The solidified alloys have been studied by electron microscopy and x-ray diffraction to determine their composition, constituent phases, and phase morphology. It has been determined that the icosahedral phase must form directly from the liquid and, at these quench rates, is always found in the presence of second or third phases. The results have been summarized in a metastable phase diagram appropriate for rapid solidification of $\text{Al}_{1-x}\text{Ru}_x$ at piston and anvil quench rates. This metastable phase diagram describes the results for Ru concentrations less than 14 at%.

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11. Microstructure of Mechanically Alloyed $\text{Fe}_{78}\text{Mo}_{10}\text{Sm}_{12}$ Magnets with the ThMn_{12} Structure (Publication 75)

C. Koestler,[†] L. Schultz,[‡] and G. Thomas

The ThMn_{12} -type $\text{Fe}_{78}\text{Mo}_{10}\text{Sm}_{12}$ magnet has been characterized by high-resolution electron microscopy, x-ray microanalysis, and microdiffraction. In general, the microstructure of the mechanically alloyed and annealed magnets consists of the tetragonal 1:12 matrix phase with an average matrix grain diameter of 200–300 nm and two rare earth-oxide phases, the SmO phase and the Sm_2O_3 phase. Microdiffraction data clearly verify the fcc structure of the single and polycrystalline SmO grains, while the Sm_2O_3 phase was found to exist only in a single-crystal hcp and monoclinic structure. In this material, no grain-boundary phases at multigrain junctions were observed. The high defect concentration in the matrix grains seems to be responsible for the pinning of the domain walls and the

good magnetic properties of the $\text{Fe}_{78}\text{Mo}_{10}\text{Sm}_{12}$ magnets. However, it was not possible to resolve magnetic domains by Lorentz imaging methods.

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12. Simulation of High-Resolution Images of Wedge-Shaped Crystals (Publication 40)

C.J.D. Hetherington, M.A. O'Keefe, and R. Kilaas

TEM specimens of semiconductor materials, prepared by cleaving on well-defined planes, have clean, flat surfaces, and the regular wedge shape means that the thickness is directly related to the distance from the edge of the specimen. The form of the high-resolution image varies across a single micrograph as the thickness and exit-surface height (i.e., focus) change, in a known way, across the specimen. Experimental images of these specimens are thus already well characterized and can be used to test the accuracy of simulated images under these conditions. This paper shows examples of experimental and simulated images and examines the success (or otherwise) of the matching for various computational procedures and model specimen parameters.

13. Simulated Image Maps for Use in Experimental High-Resolution Electron Microscopy (Publication 51)

M.A. O'Keefe, U. Dahmen, and C.J.D. Hetherington

A "map" of all possible high-resolution images may be simulated for a crystalline specimen in a chosen orientation for any particular transmission electron microscope (HRTEM). These maps, an example of which is given in Figure 13-1, are useful during experimental high-resolution electron microscopy and make it possible to locate optimum imaging conditions even for foil thicknesses beyond the weak-phase object limit. Although defects such

Figure 13-1. Image map for [110] aluminum under ARM conditions. Defocus values (horizontal) are from 0 to -1400 Å in steps of -100 Å. Thickness values (vertical) are from 20 Å to 440 Å in steps of 20 Å. Atom positions (black dots) are shown top left. Largest region with "faithful" images in the "white atom" region in center of top half of map, and extending from -900 Å defocus at 20 Å thickness to -500 Å defocus at 200 Å thickness. (XBB 890-10595)

as grain boundaries are not generally periodic, image maps of perfect crystals can be used to optimize the defect contrast during operation of the microscope by reference to the image of the perfect crystal neighboring the defect.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. S.M. Anlage, B. Fultz, and K. M. Krishnan, "Icosahedral Phase Formation in Rapidly Quenched Aluminum-Ruthenium Alloys," *J. Mat. Res.* **3**, 421 (1988).
2. P. Askenazy, E. Kamenetzky, L. Tanner, and W. Johnson, "Deformation-Induced Amorphization of CuTi_2 Microcrystals in an Amorphous Matrix," *J. Less-Common Metals* **140**, 149 (1988).
3. H.W. Chan, D.G. Howitt, and A. Harker, "Microstructures of Simulated ICPP Nuclear Waste," *J. Am. Ceram. Soc.* **72**, 1040 (1989).
4. U. Dahmen, "Transmission Electron Microscopy Characterization of Precipitates," *Ultramicrosc.* **30**, 102 (1989); LBL-24660.

5. U. Dahmen and K.H. Westmacott, "The Use of Heteroepitaxy in the Fabrication of Bicrystals for the Study of Grain Boundary Structure," *Scripta Metall.* **22**, 1673 (1988); LBL-25602.
6. U. Dahmen, C.J.D. Hetherington, P. Pirouz, and K.H. Westmacott, "The Formation of Hexagonal Silicon at Twin Intersections," *Scripta Metall.* **23**, 269 (1989); LBL-26233.
7. A.G. Fox, M.A. O'Keefe, and M.A. Tabbernor, "Relativistic Hartree-Fock X-Ray and Electron Atomic Scattering Factors at High-Angles," *Acta Crystallogr. A* **45**, 786 (1989); LBL-26387.
8. J.M. Howe, D.E. Laughlin, and A.K. Vasudevan, "High-Resolution TEM Investigation of the δ'/θ' Precipitate Structure in an Al-2Li-1Cu Alloy," *Philos. Mag. A* **57**, 955 (1988).
9. J.M. Howe, J. Lee, and A.K. Vasudevan, "The Structure, Transformation and Deformation Behavior of T_1 Precipitate Plates in an Al-2Li-1Cu Alloy," *Metall. Trans.* **19A**, 2911 (1988).
10. J.M. Howe and G.J. Mahon, "High-Resolution Transmission Electron Microscopy of Precipitate Plate Growth by Diffusional and Displacive Transformation Mechanisms," *Ultramicrosc.* **30**, 132 (1989).
11. C. Koestler, R. Ramesh, C.J. Echer, G. Thomas, and J. Wecker, "Microstructure of Melt Spun Nd-Fe-Co-B Magnets," *Acta Metall.* **37**, 1945 (1989); LBL-26156.
12. K. Krishnan, "Site Occupancy/Valence Measurements using Channelling and Related Effects in Microanalysis," *Mat. Sci. Eng.* **B3**, 397 (1989); LBL-26580.
13. Q. Li, J. Megusar, L.J. Masur, and J.A. Cornie, "A High Resolution Transmission Electron Microscopy Study of the SiC Coated Graphite Fiber/Aluminum Composite," *Mat. Sci. Eng.* **117A**, 199 (1989).
14. Z. Liliental-Weber, M.A. O'Keefe, and J. Washburn, "Inversion Boundaries in GaAs Grown on Si," *Ultramicrosc.* **30**, 20 (1989); LBL-25779.
15. Z. Liliental-Weber, N. Newman, J. Washburn, E.R. Weber, and W.E. Spicer, "The Influence of Contamination on the Structure and Barrier Height in Cr/GaAs Schottky Contacts," *Appl. Phys. Lett.* **54**, 356 (1989); LBL-25990.
16. G.J. Mahon, J.M. Howe, and S. Mahajan, "Atomic-Resolution TEM Investigation of the {225} Austenite/Martensite Interface in an Fe-8Cr-1C Alloy," *Philos. Mag. Lett.* **59**[6], 273 (1989).
17. A. Meike, "In situ Deformation of Micas: A High-Voltage Electron-Microscope Study," *Amer. Mineral.* **74**, 780 (1989).
18. V. Radmilovic, G. Thomas, G.J. Shiflet, and E.A. Starke, Jr., "On the Nucleation and Growth of Al_2CuMg (S') in Al-Li-Cu-Mg and Al-Cu-Mg Alloys," *Scripta Metall.* **23**, 1141 (1989); LBL-26629.
19. V. Radmilovic, A.G. Fox, R.M. Fisher, and G. Thomas, "Lithium Depletion in Precipitate Free Zones (PFZs) in Al-Li Base Alloys," *Scripta Metall.* **23**, 75 (1989); LBL-25603.
20. R. Ramesh, G. Thomas, S.M. Green, M.L. Rudee, Y. Mei, and H.L. Luo, "Bi-Ca-Sr-Cu-O Superconductors: the

- Connectivity Issue," *IEEE Trans. Magn.* **25**, 2360 (1989); LBL-25842.
21. R. Ramesh, G. Thomas, R.L. Meng, P.H. Hor, and C.W. Chu, "Electron Microscopy of a Gd-Ba-Cu-O Superconductor," *J. Mater. Res.* **4**, 515 (1989); LBL-25405.
 22. R. Ramesh, G. van Tendeloo, G. Thomas, S.M. Green, and H.L. Luo, "New Modulated Structure in a Pb-Doped Bi-Ca-Sr-Cu-O Superconductor," *Appl. Phys. Lett.* **53**, 2220 (1988).
 23. R. Ramesh, D.M. Hwang, T. Venkatesan, T.S. Ravi, L. Nazar, A. Inam, X.D. Wu, B. Dutta, G. Thomas, A.F. Marshall, and T.H. Geballe, "Direct Observation of Structural Defects in Laser-Deposited Superconducting Y-Ba-Cu-O Thin Films," *Science* **247**, 57 (1990).
 24. P. Sheldon, M.M. Al-Jassim, K.M. Jones, J.P. Goral, and B.G. Yacobi, "Structural and Electrical Characterization of InAs Grown on GaAs substrates grown by MBE," *J. Vac. Sci. Technol.* **A7**, 770 (1989).
 25. M.J. Witcomb, U. Dahmen, and K.H. Westmacott, "The Coprecipitation of Cr_3P and Cr in Cu," *Ultramicrosc.* **30**, 143 (1989); LBL-24953.
 26. H.W. Zandbergen, C.J.D. Hetherington, and R. Gronsky, "Sample Preparation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-8}$ for High Resolution Electron Microscopy," *J. Superconductivity* **1**, 26 (1988); LBL-24614.
 27. H.W. Zandbergen and G. Thomas, "Grain Boundaries in Sintered $\text{YBa}_2\text{Cu}_3\text{O}_{7-8}$," *Acta Crystallogr.* **A44**, 772 (1988); LBL-24603.
 28. H.W. Zandbergen and G. Thomas, "HREM Investigations of Defects in Sintered $\text{YBa}_2\text{Cu}_3\text{O}_{7-8}$," *phys. stat. sol. (a)* **107**, 825 (1988).
 29. H.W. Zandbergen, R. Gronsky, and G. Thomas, "Atomic Structure of (001) Grain Boundaries and (001) Surfaces in $\text{YBa}_2\text{Cu}_3\text{O}_{7-8}$," *J. Microscopie et de Spectroscopie Electronique* **13**, 307 (1988); LBL-25800.
 30. J. Kulik, D. Gratias, and D. de Fontaine, "Short-Range Order in Electron-Irradiated Cu-Pd: Fluctuations in a Nonequilibrium Steady State," *Phys. Rev. B* **40**, 8607 (1989); LBL-26778.
 34. M. Sarikaya, "Atomic Resolution Microscopy in Materials," in *Ceramic Transactions, Proc. Adv. Characterization Techniques for Ceramics*, Vol. 5, W. Young, G. Pike, and G.L. McVay, Eds., American Ceramic Society, 1989, p. 247.
 35. M.M. Al Jassim, J.P. Goral, P. Sheldon, and K.M. Jones, "The Heteronucleation of and Defect Generation in MBE-Grown InAs Layers," in *Proc. 1989 Mater. Res. Soc. Fall Meeting*, Vol. 144, 1989, p. 183.
 36. U. Dahmen and K.H. Westmacott, "Using Crystallographic Symmetry in Diffraction and Contrast Analysis," in *Proc. 47th Ann. Meeting EMSA*, San Antonio, TX, Aug. 1989, G.W. Bailey, Ed., San Francisco Press, 1989, p. 504; LBL-26920.
 37. U. Dahmen, J. Douin, C. Hetherington, and K.H. Westmacott, "High Resolution Electron Microscopy of Interfaces in Topotaxial and Epitaxial Reactions," *MRS Symp. High Resolution Microscopy of Materials* **139**, 87 (1989); LBL-26545.
 38. T.A. Epicier, H. Wohlfromm, and G. Thomas, "Dislocation Analysis in Al_2TiO_5 ," in *Proc. 47th Ann. Meeting EMSA*, San Antonio, TX, Aug. 1989, G.W. Bailey, Ed., San Francisco Press, 1989, p. 422; LBL-26894.
 39. T.A. Epicier and G. Thomas, "Conditions for Atomic Imaging of Mullite," in *Proc. 47th Ann. Meeting EMSA*, San Antonio, TX, Aug. 1989, G.W. Bailey, Ed., San Francisco Press, 1989, p. 418; LBL-26893.
 40. C. Hetherington, M.A. O'Keefe, and R. Kilaas, "Simulation of High Resolution Images of Wedge-Shaped Crystals," in *Proc. TMS Annual Meeting*, Las Vegas, NV, Feb. 1989, p. 185; LBL-25796.
 41. C.J.D. Hetherington, E.C. Nelson, K.H. Westmacott, R. Gronsky, and G. Thomas, "The Berkeley Atomic Resolution Microscope—an Update," in *Proc. MRS Fall Meeting*, Boston, MA, Nov. 28–Dec. 3, 1988, p. 277; LBL-25797.
 42. C.J.D. Hetherington, U. Dahmen, P. Pirouz, and K.H. Westmacott, "HREM of Twin Intersections in Silicon," in *Proc. 47th Ann. Meeting EMSA*, San Antonio, TX, Aug. 1989, G.W. Bailey, Ed., San Francisco Press, 1989, p. 132; LBL-26929.
 43. T. Huynh and G. Thomas, "Characterization of Barium Ferrite Recording Materials," in *Proc. MRS Internat. Mtg. on Adv. Mats.*, Vol. 11, 1989, p. 229; LBL-25359.
 44. E. Kamenetzky, M. Wall, R. Castro, and L.E. Tanner, "The Preparation of Mechanically Alloyed Powders for TEM Examination," *Mat. Res. Soc. Symp. Proc.* **115**, 167 (1988).
 45. R. Kilaas and M.A. O'Keefe, "The Design of a Computer System for Image Simulation and Image Processing of High Resolution Electron Micrographs," in *Proc. Symp. Computer Simulation of EM Diffraction*, Las Vegas, NV, Feb. 28–Mar. 3, 1989, p. 183; LBL-27444.
 46. K.M. Krishnan, "Spectroscopy: Electron Energy-Loss Spectroscopy: Fundamentals and Applications in the Characterization of Minerals," in *Structures and Active Sites of Minerals*, Ann. Mtg. Amer. Chem. Soc. Symp. Series, Coyne, McKeever, and Blake, Eds., 1988, p. 54; LBL-26222.

Other Publications

31. L.B. Blackburn and E.A. Starke, Jr., "Effect of In Additions on Microstructure Mechanical Property Relationships for an Al-Cu-Li Alloy," in *Aluminum-Lithium Alloys*, Proc. 5th Internat. Al-Li Conf., Williamsburg, VA, Mar. 1989, T.H. Sanders and E.A. Starke, Jr., Eds., 1989, p. 413.
32. R. Ramesh, S.M. Green, and G. Thomas, "Microstructure Property Relationships in the Bi(Pb)-Sr-Ca-Cu-Co Ceramic Superconductors," in *Studies of High Temperature Superconductors*, A.V. Narlikar, Ed., Vol. 4, Nova Science Publishers, Inc., Commack, NY, Oct. 1989; LBL-27829.
33. M.R. Libera and M. Chen, "The Effect of an Aluminum Heat-Sink Layer on the Laser-Induced Amorphization of $\text{SiO}_x/\text{TeGeSn}/\text{SiO}_x$ Phase-Change Recording Films," in *Optical Materials: Processing and Science*, D.B. Poker, et al., Eds; Mat. Res. Soc., Pittsburgh, 1989, p. 203.

47. K.M. Krishnan, "Microanalytical and Structural Characterization of Optical Materials by Electron Microscopy and Related Spectroscopies," in *Proc. MRS*, Vol. 152, San Diego, April 24, 1989, p. 151; LBL-27094.
48. A. Meike, "Specimen Cage Modification for TEM *in-situ* Shearing," *Mat. Res. Soc. Symp. Proc.* **115**, 211 (1988).
49. M.L. Sattler and M.A. O'Keefe, "HRTEM Simulation of Interfacial Structure in Amorphous Multilayers," in *Proc. 47th Ann. Meeting EMSA*, San Antonio, TX, Aug. 1989, G.W. Bailey, Ed., San Francisco Press, Inc., 1989, p. 466.
50. M.A. O'Keefe and R. Kilaas, "Current and Future Directions of On-Line Transmission Electron Microscope Image Processing and Analysis," in *Proc. 47th Ann. Meeting EMSA*, San Antonio, TX, Aug. 1989, G.W. Bailey, Ed., San Francisco Press, Inc., 1989, p. 49; LBL-26926abs.
51. M.A. O'Keefe, U. Dahmen, and C.J.D. Hetherington, "Simulated Image Maps for Use in Experimental High-Resolution Microscopy," in *Proc. MRS Fall Meeting*, Boston, MA, Nov. 28-Dec. 3, 1989, p. 141; LBL-27503.
52. F. Ponce and C.J.D. Hetherington, "HREM at Orthogonal Projections of GaAs Islands on Silicon," in *Proc. 47th Ann. Meeting EMSA*, San Antonio, TX, Aug. 1989, G.W. Bailey, Ed., San Francisco Press, Inc., 1989, p. 586; LBL-27321.
53. M. Sarikaya, "Characterization of Advanced Materials by High Resolution Transmission Electron Microscopy," in *Proc. MRS*, Seattle, WA, Aug. 29-Sept. 2, 1987, 1988, p. 211.
54. D. Schryvers, L.E. Tanner, and G. van Tendeloo, "Premartensitic Microstructures as Seen in the High-Resolution Electron Microscope: A Study of Ni-Al Alloy," NATO/ASI meeting on *Phase Stability*, A. Gonis and M. Stocks, Eds., Kluwer Acad., Dordrecht, The Netherlands, p. 599.
55. D. Schryvers, L.E. Tanner, and S.M. Shapiro, "Electron Microscopy and Neutron Scattering Studies of Premartensitic Behavior in a Ni-Al b-Phase Alloy," in *Proc. MRS Symp. on Shape-Memory Materials*, K. Otsuka and K. Shimizu, Eds., Vol. 9 of *Ser. Internat. Meetings on Advanced Materials*, Tokyo, 1988-89, MRS, Pittsburgh, 1989, p. 35.
56. S. Tanaka, H. Usui, U. Dahmen, K.H. Westmacott, and I. Yamada, "Microstructure of Epitaxial Al Films Deposited on Si by ICB Method," in *Proc. 12th Symp. ISIJAT'89*, Tokyo, Japan, June 5-7, 1989, p. 281.
57. L.E. Tanner, "On the Systematics of Phase Transformations in Metallic Alloys," in *Proc. Symp. on Competing Interactions and Microstructures Statics and Dynamics*, Springer Solid State Sciences Series, R. LeSar and A.R. Bishop, Eds., Vol. 27, Springer-Verlag, Berlin, 1989, p. 74.
58. G.J. Thomas, R.W. Siegel, and J. Eastman, "High Resolution Electron Microscopy of Grain Boundaries in Nanophase Palladium," *Mat. Res. Soc. Symp. Proc.* **153**, 13 (1989).
59. G. Thomas, "High Voltage High Resolution Electron Microscopy," in *Atti del XVII Congresso di M.E.*, Lecce, Italy, Sept. 1989, p. 13.
60. K.H. Westmacott and U. Dahmen, "Fundamental Studies of Grain Boundary Structure and Properties in ICB Aluminum," in *Proc. 12th Symp. ISIJAT'89*, Tokyo, Japan, June 5-7, 1989, T. Takagi, Ed., p. 255; LBL-27187.
61. H.W. Zandbergen, R. Gronsky, and G. Thomas, "The Atomic Structure at Grain Boundaries, the Cause of Low Current in Sintered $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$," *Inst. Phys. Conf. Ser.* No. 93: Vol. 2, Chap. 6, EUREM 88, York, England, 1988; LBL-25578.
62. A.M.T. Motta (Ph.D. Thesis), "Crystalline-Amorphous Transformation of Precipitates in Zircaloy Under Electron Irradiation."
63. R.J. Spontak (Ph.D. Thesis), "Applications of TEM in Characterizing the Microstructures of Phase-Separated Block Copolymers."
64. K.H. Westmacott and U. Dahmen, "A Comparative HVEM Study of ICB-Deposited Films," in *Proc. 47th Ann. Meeting EMSA*, San Antonio, TX, Aug. 1989, G.W. Bailey, Ed., San Francisco Press, 1989, p. 642; LBL-26919.

LBL Reports

65. U. Dahmen, C. Hetherington, M.A. O'Keefe, K.H. Westmacott, M.J. Mills, M.S. Daw, and V. Vitek, "Atomic Structure of a $\Sigma 99$ Grain Boundary in Aluminum: a Comparison Between Atomic Resolution Observation, Pair Potential and Embedded Atom Simulations," submitted to *Phys. Rev. Lett.*; LBL-28123.
66. K.H. Westmacott and U. Dahmen, "High Voltage/High Resolution Studies of Metal and Semiconductor Interfaces," in *Proc. Int. Symp. on EM in Plasticity*, Holzhau, German Democratic Republic, Oct. 8-13, 1989 (in press); LBL-26274.
67. U. Dahmen and K. H. Westmacott, "Problems of Enclosed Crystal Interfaces," in *Proc. Indo-U.S. Workshop on Interfaces: Structure and Properties*, Bangalore, India, Nov. 30-Dec. 3, 1989 (in press); LBL-28388.
68. K.H. Westmacott and U. Dahmen, "Hot Stage Studies of Homophase and Heterophase Interfaces," in *Proc. Indo-U.S. Workshop on Interfaces: Structure and Properties*, Bangalore, India, Nov. 30-Dec. 3, 1989 (in press); LBL-27388.
69. U. Dahmen and K.H. Westmacott, "Control of Interfaces for TEM Analysis," submitted to *J. Electr. Micr. Techniques*; LBL-27259.
70. U. Dahmen, K.H. Westmacott, P. Pirouz, and R. Chaim, "The Martensitic Transformation in Silicon: 2, Crystallographic Analysis," *Acta Metall.* (in press); LBL-27072.
71. U. Dahmen, M.J. Witcomb, and K.H. Westmacott, "Aspects of Faceting in the Study of Precipitate Interfaces," submitted to *J. Phys. Colloque*; LBL-27834.
72. J. Douin, U. Dahmen, and K.H. Westmacott, "On the Formation of Twinned Precipitates in Al-Ge Alloys," submitted to *Philos. Mag.*; LBL-27258.
73. T. Epicier, M.A. O'Keefe, and G. Thomas, "Atomic Imaging of 3:2 Mullite," accepted by *Acta Crystallogr.*; LBL-27169.
74. H.W. Zandbergen, G.F. Holland, P. Tejedor, R. Gronsky, and A.M. Stacy, "A Study of Mixed Phase Behavior in the Lanthanide-Substituted Superconducting Oxide

ErBa₂Cu₃O₇," to be published in a special issue of "Advanced Ceramic Materials," J. Am. Ceram. Soc.; LBL-23566.

75. C. Koestler, L. Schultz, and G. Thomas, "Microstructure of Mechanically Alloyed Fe₇₈Mo₁₀Sm₁₂-Magnets with the ThMn₁₂-Structure," submitted to J. Appl. Phys.; LBL-28062.

Invited Talks

76. U. Dahmen (speaker) and K.H. Westmacott, "High Resolution Imaging of Near-Sigma $\langle 110 \rangle$ Boundaries in Aluminum," Proc. EMSA, Durban, South Africa, Dec. 1988.
77. K.H. Westmacott (speaker) and U. Dahmen, "Fundamental Studies of Grain Boundary Structure and Properties in ICB Aluminum," ISIAT'89 Conf., Tokyo, Japan, June 5-7, 1989.
78. K.H. Westmacott and U. Dahmen, "The NCEM," TMS Fall Meeting, Chicago, IL, Sept. 25-28, 1988; LBL-25839abs.
79. K.H. Westmacott, "Structure and Properties of Al Bicrystals," Max Planck Institute, Stuttgart, Federal Republic of Germany, Oct. 4, 1989.
80. K.H. Westmacott, "The Role of Twinning in Precipitate Formation in Al-Ge," Halle University, Halle, Federal Republic of Germany, Oct. 6, 1989.
81. K.H. Westmacott (speaker) and U. Dahmen, "High Voltage/High Resolution Studies of Metal and Semiconductor Interfaces," International Symposium of Electron Microscopy in Plasticity, Holzhausen, German Democratic Republic, Oct. 8-13, 1989.
82. K.H. Westmacott (speaker), U. Dahmen, and M.J. Witcomb, "Carbides of Platinum," Leo Brewer Symposium on High Temperature and Materials Chemistry, Berkeley, CA, Oct. 24-25, 1989; LBL-27905.
83. K.H. Westmacott (speaker) and U. Dahmen, "Hot Stage Studies of Homophase and Heterophase Interfaces," Indo-U.S. Workshop on Interfaces: Structure and Properties, Bangalore, India, Nov. 30-Dec. 3, 1989.
84. K.H. Westmacott, "Facilities and Research at the NCEM," Electrochemical Society, Palo Alto, CA, Mar. 8, 1989.
85. K.H. Westmacott, "Research at the NCEM," American Society of Metals, San Diego, CA, Apr. 13, 1989.
86. K.H. Westmacott, "Recent Applications of HREM," University of Birmingham, UK, May 4, 1989.
87. U. Dahmen (speaker) and K.H. Westmacott, "Problems of Enclosed Crystal Interfaces," Indo-U.S. Workshop on Interfaces: Structure and Properties, Bangalore, India, Nov. 30-Dec. 3, 1989.
88. U. Dahmen, M. Witcomb, and K.H. Westmacott, "Morphology and Interface Structure of Lath-Shaped Precipitates in Cu-Cr Alloys," Annual TMS Meeting, Las Vegas, NV, Feb. 1989.
89. U. Dahmen, "Crystal Mirrors as Markers in Microscopy of Materials," Northern California Section, EMSA, San Francisco, CA, Mar. 1989.
90. U. Dahmen, "Electron Microscopy Characterization of Defects and Precipitates," Summer School on Electron Microscopy, Stockholm, Sweden, Aug. 20-25, 1989.
91. U. Dahmen (speaker), M.J. Witcomb, and K.H. Westmacott, "Aspects of Faceting in the Study of Precipitate Interfaces," International Congress on Intergranular and Interphase Boundaries in Materials, Paris, Sept. 4-8, 1989.
92. U. Dahmen, V. Vitek, M.A. O'Keefe, and K.H. Westmacott, "The Structure of Asymmetric $\Sigma 17 \langle 110 \rangle$ Tilt Boundaries in Al: Comparison of Experimental Observation and Atomistic Calculation," International Congress on Intergranular and Interphase Boundaries in Metals, Paris, Sept. 4-8, 1989; LBL-27185.
93. U. Dahmen, "Crystallographic Aspects of Ledge Growth," International Symposium on Ledges, TMS/AIME Annual Meeting, Indianapolis, IN, Oct. 2-6, 1989; LBL-27195abs.
94. U. Dahmen, "TEM Studies of Interfaces and Phase Transformations," Exxon Research Laboratories, Annandale, NJ, Oct. 6, 1989.
95. U. Dahmen, "Aspects of Symmetry in Phase Transformations," Department of Materials Science, University of California at Berkeley, Oct. 12, 1989.
96. G. Thomas, "High Resolution Electron Microscopy of Ferrites and Cuprates," 5th International Ferrite Conference, Bombay, India, Jan. 10-15, 1989.
97. R. Ramesh, C.J.D. Hetherington, G. Thomas (speaker), S.M. Green, and H.L. Luo, "Transmission Electron Microscopy of High T_c Bi-Ca-Sr-Cu-O Superconductor," 5th International Ferrite Conference, Bombay, India, Jan. 10-15, 1989.
98. C.J.D. Hetherington and G. Thomas, "Atomic Imaging and Interfacial Analysis," Acta/Scripta Metallurgica Conference on Bonding, Structure, and Mechanical Properties of Metal/Ceramic Interfaces, University of California, Santa Barbara, Jan. 16-19, 1989.
99. G. Thomas, "Electron Microscopy and Microanalysis of Fine Ceramics," Mitsubishi Mining and Cement Co., Chichibu, Japan, Feb. 20, 1989.
100. G. Thomas, "Electron Microscopy and Microanalysis of Magnetic Materials," Showa Denko K.K. Co., Tokyo, Japan, Feb. 21, 1989.
101. R. Ramesh, G. Thomas (speaker), S.M. Green, and H.L. Luo, "Transmission Electron Microscopy of High T_c BSCCO Superconductors," TMS-AIME Spring Meeting, Las Vegas, NV, Feb. 28-Mar. 1, 1989.
102. C. Koestler, R. Ramesh, C. J. Echer, J. Wecker, and G. Thomas (speaker), "Microstructure of Melt Spun Fe-Co-Nd-B Magnets," TMS-AIME Spring Meeting, Las Vegas, NV, Feb. 28-Mar. 1, 1989.
103. G. Thomas, "Transmission Electron Microscopy: Imaging of Materials," International Conference on Scanning EM West, Long Beach, CA, Apr. 4-7, 1989.
104. G. Thomas, "Electron Microscopy and Microanalysis of Structural Ceramics," Tosoh Corp., Tokyo, Japan, May 31, 1989.
105. G. Thomas, "HREM of Warm Superconductors," Matsushita Electric Co., Osaka, Japan, May 31, 1989.
106. G. Thomas, "Characterization of Advanced Materials by Electron Microscopy," University of Lyons, France, June 7, 1989; 12th ICXOM Conference, Cracow, Poland, Aug. 28-

- Sept. 1, 1989; Carnegie Mellon University, Pittsburgh, PA, Sept. 12, 1989.
107. G. Thomas, "Atomic Imaging of Inorganic Materials," 3rd Balkan Congress on Electron Microscopy, Athens, Greece, Sept. 18-23, 1989.
 108. G. Thomas, "High Voltage, High Resolution Electron Microscopy," SIME ATTI Congress, Lecce, Italy, Oct. 2-6, 1989.
 109. G. Thomas, "Characterization of Advanced Ceramic Materials by Electron Microscopy," First Japan SAMPE Conference, Chiba, Japan, Nov. 28-Dec. 1, 1989.
 110. K. Krishnan, "Microanalytical and Structural Characterization of Optical Materials by Electron Microscopy and Related Spectroscopies," MRS Spring Meeting of Optical Materials: Processing and Science, San Diego, CA, Apr. 24, 1989.
 111. K. Krishnan, "Channelling and Related Effects in Electron Microscopy: The Current Status," 8th Pfeifferkorn Meeting on Fundamental Beam Solid Interactions for Microscopy, Microanalysis and Lithography, Salt Lake City, UT, May 8, 1989.
 112. K. Krishnan, "Analytical Electron Microscopy and Related Spectroscopies," (two lectures), Transmission Electron Microscopy: Problem Solving in Material Science Summer School, The Royal Institute of Technology, Stockholm, Sweden, Aug. 24, 1989.
 113. M.A. O'Keefe, "High-Resolution TEM Image Analysis at the National Center for Electron Microscopy," Instituto de Fisica, Universidad Nacional Autonoma de Mexico, Aug. 1989.
 114. M.A. O'Keefe, "High Resolution TEM Image Simulation: Theory and Practice," Instituto de Fisica, Universidad Nacional Autonoma de Mexico, Aug. 1989.
 115. M.A. O'Keefe, "Image Analysis at the National Center for Electron Microscopy at Berkeley," Instituto de Fisica, Universidad Nacional Autonoma de Mexico, Oct. 18, 1989.
 116. C.J.D. Hetherington, "Electron Microscopy of Chromium Thin Films," West Coast Microbeam Analysis Society, Redwood City, CA, Jan. 20, 1989.
 117. C.J.D. Hetherington, "Introduction to Electron Microscopy," Science for Science Teachers, Lawrence Hall of Science, Berkeley, CA, July 10, 1989.
 118. C.J.D. Hetherington, "Applications of HREM on the ARM-1000," Argonne National Laboratory, Argonne, IL, May 23, 1989; Northwestern University, Chicago, IL, May 24, 1989; IBM, Yorktown Heights, NY, May 25, 1989; ATT Bell Laboratories, Murray Hill, NJ, May 26, 1989; Bellcore, Annandale, NJ, May 30, 1989; North Carolina State University, Raleigh, May 31, 1989.
 119. R. Kilaas, "The Design of a Computer System for Image Simulation and Image Processing of High Resolution Electron Micrographs," The Minerals, Metals & Materials Society Meeting, Las Vegas, NV, Feb. 28-Mar. 3, 1989.

Gas-Solid Reactions*

James W. Evans, Investigator

INTRODUCTION

This research is concerned with reactions between gases and solids in materials science. In many such reactions of actual or potential technological significance (e.g., the reaction of tungsten hexafluoride with silicon in the chemical vapor deposition on tungsten during silicon semiconductor processing), new solid phases appear. The nucleation, growth, epitaxy, and crystallinity of these phases, as well as changes to the microstructure of reactant phases, are the focus of this research.

The principal experimental tools are the high-voltage transmission electron microscopes at Berkeley. Environmental cells located within such devices permit the reaction between a gas and a solid to be observed at high magnification. Selected-area electron diffraction is carried out simultaneously and provides the identification of reaction products as well as information on their crystallinity and orientation to the solid reactant. Other modern analysis techniques, such as Rutherford backscattering spectroscopy (RBS) and scanning electron microscopy (SEM), are also used in this investigation.

1. *In Situ* Observations of the Orthorhombic-Tetragonal Phase Transformation in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Publication 1)

O.R. Monteiro, J.W. Evans, and S. Johnson[†]

Some *in situ* heat treatments of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ at temperatures between 25°C and 500°C and oxygen pressures of 10 torr have been carried out. It was found that the original orthorhombic OI $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ transforms into the OII phase (still orthorhombic, but with a doubling of the a-axis, and with a $\delta = 0.5$) at about 250°C. As the temperature is increased further, the tetragonal phase of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ forms. This is evident in the sequence of electron diffraction patterns of Figure 1-1. Faint streaks initially present in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ become stronger as the temperature is raised to 473 K. These streaks are

Figure 1-1. Sequence of diffraction patterns in a [021] zone axis, obtained at different temperatures (shown in each pattern) and in 10 torr O_2 . The arrows point to the diffuse streaks, which become spots at 523 K, indicating the formation of OII phase. As temperature increases, the tetragonal phase is formed. (XBB 890-10914)

characteristic of the presence of the OII phase dispersed in the OI matrix. By 523 K the streaks have become spots, indicating considerable transformation to the OII phase. The tetragonal phase is evident in the diffraction pattern at 623 K. As the tetragonal phase is slowly cooled to room temperature, the orthorhombic phase OI reappears. Cycling the temperature repeatedly has indicated the regenerability of the OI phase.

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2. Model of Internal Gettering from Low-Temperature Fe Precipitation Kinetics in Czochralski Silicon (Publication 2)

D. Gilles,[†] E.R. Weber,[†] S. Hahn,[‡] O.R. Monteiro, and K.H. Choll

Results are presented on low-temperature precipitation of Fe in Cz-Si after different annealing treatments for precipitation of oxygen. It is concluded that internal gettering requires supersaturation and a sufficient diffusivity of the metal impurity. The effectiveness of the process depends on the density of heterogeneous nucleation sites, which were found to be determined by oxygen precipitates. The Fe precipitation kinetics is used to

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determine O-precipitate densities after various two-step annealings.

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^{||}Permanent address: Lucky Advanced Materials, Inc., Gumi, Kyungsangbuk-Do, Republic of Korea.

3. Work in Progress

In situ and *ex situ* electron microscopy techniques are being used to examine the reaction between tungsten

hexafluoride and silicon as well as the oxidation of porous silicon.

1989 PUBLICATIONS AND REPORTS

LBL Reports

1. O.R. Monteiro, J.W. Evans, and S. Johnson, "In-Situ Observations of the Orthorhombic-Tetragonal Phase Transformation in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$," LBL-28286.
2. D. Gilles, E.R. Weber, S. Hahn, O.R. Monteiro, and K. Cho, "Model of Internal Gettering from Low-Temperature Fe Precipitation Kinetics in Czochralski Silicon," LBL-28281.

Local Atomic Configurations in Solid Solutions*

Didier de Fontaine, Investigator

INTRODUCTION

This investigation is concerned with ordering phenomena in alloys, and the recent emphasis has been on long-period ordered superstructures (modulated structures) in binary fcc alloys. Two systems have been studied in detail: Cu-Pd and Ag-Mg. Structural observations have been carried out using the Atomic Resolution Microscope at LBL's National Center for Electron Microscopy (NCEM), and the nature of the periodic antiphase boundaries present in these alloys has been characterized. In addition, a systematic investigation of long- and short-range order in Cu-Pd has been undertaken using *in situ* variation of temperature and radiation dose in the High Voltage Electron Microscope at NCEM. Other work on the Cu-Pd system, using standard electron microscopy techniques, is directed toward clarification of the equilibrium phase diagram. A statistical mechanics model for modulated structures in alloys has been proposed and solved within the mean-field approximation. Results show excellent agreement with observed long-period superstructures in Cu-Pd. Considerable effort on this project has been redirected toward the theoretical study of phase equilibria in high- T_c superconductors. Results are described in the Alloy Theory section of this Annual Report. Both projects are now merging into a single one.

1. A Gorsky-Bragg-Williams Approach to the Study of Long-Period Superlattice Phases in Binary Alloys (Publication 1)

G. Ceder, M. De Graef,[†] L. Delaey,[‡] J. Kulik,[‡] and D. de Fontaine

The influence of the shape of the reciprocal-space potential on the relative stability of long-period superlattice (LPS) phases in binary alloys is discussed in a Gorsky-Bragg-Williams approximation. First, for a certain class of LPS phases, the set of pair-interaction parameters is reduced to a smaller set of parameters that characterize only the essential aspects of the reciprocal-space potential.

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Minimization of the free energy for different LPS phases is then used to extract some general tendencies, such as the change of wave vector toward the potential minimum (with increasing temperature) and the increasing stability of complex phases with deepening of the potential minimum.

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2. Short-Range Order in Electron-Irradiated Cu₃Pd: Fluctuations in a Nonequilibrium Steady State (Publication 2)

J. Kulik,[†] D. Gratias,[‡] and D. de Fontaine

Electron-diffraction results on specimens of Cu-Pd alloys under irradiation with 1.5-MeV electrons at temperatures from 200 to 400 K are presented. The irradiation induces atomic mobility through the production of point defects but maintains the system in a disordered state despite a long-range ordered phase being the equilibrium state. The presence of short-range order (SRO) is detected in electron-diffraction data. SRO in Cu-Pd is characterized by peaks of intensity that flank the 100 and equivalent positions in the Brillouin zone, removed from those positions by a distance q_m . The quantity q_m varies with Pd content and also with the temperature at which the system is irradiated. An analogy is drawn with an equilibrium statistical model.

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3. *Ab Initio* Study of the Cu-Pd One-Dimensional Long-Period Superstructure Phase Diagram (Publication 3)

G. Ceder, D. de Fontaine, H. Dreyssé,[†] D.M. Nicholson,[‡] G.M. Stocks,[‡] and B.L. Gyorffy^{||}

The fcc superstructure phase diagram for Cu-Pd is calculated by means of isotropic effective interactions derived from an *ab initio* Korringa-Kohn-Rostoker coherent-potential-approximation electronic-structure calculation. We prove the existence of a region in which one-dimensional long-period superstructures are stable. This region is composed of several single-phase fields in which the modulation period is constant and in close agreement with results from high-resolution electron microscopy. The change from wavy antiphase boundaries at low Pd concentration to sharp antiphase boundaries at

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Determination by transmission electron microscopy of the fcc portion of the Cu-Pd phase diagram has been completed (see Figure 4-1); a paper will be submitted shortly. Further studies in this system by electron-energy-loss spectroscopy (EELS) have been initiated.

1. G. Ceder, M. De Graef, L. Delaey, J. Kulik, and D. de Fontaine, "A Gorsky-Bragg-Williams Approach to the Study of Long Period Superlattice Phases in Binary Alloys," *Phys. Rev. B* **39**, 381 (1989); LBL-26724.
2. J. Kulik, D. Gratias, and D. de Fontaine, "Short Range Order in Electron Irradiated Cu_3Pd : Fluctuations in a Non-equilibrium Steady State," *Phys. Rev. B* **40**, 8607 (1989); LBL-26778.

3. G. Ceder, D. de Fontaine, H. Dreyssé, D.M. Nicholson, G.M. Stocks, and B.L. Gyorffy, "*Ab Initio* Study of the Cu-Pd One-Dimensional Long Period Superstructure Phase Diagram," submitted to *Acta Metall.*; LBL-28404.

Figure 4-1. The Cu-rich portion of the Cu-Pd phase diagram determined during a recent TEM study of phase transformations in Cu-Pd alloys. The ordered B2 phase region as evaluated by other workers has also been included. (XBL 901-5718)

Alloy Theory*

Didier de Fontaine and Leo M. Falicov, Investigators

INTRODUCTION

Temperature-composition phase diagrams are of great practical interest as they constitute useful "maps" of thermodynamic systems such as binary, ternary,..., alloys. These diagrams are generally determined experimentally, but the exciting possibility now exists of deriving certain classes of phase diagrams virtually from first principles. This possibility rests on the very significant advances that have been made recently in the two relevant areas of alloy theory—electronic-band-structure calculations and statistical thermodynamics. The purpose of this project is to combine the latest electronic structure and statistical thermodynamic techniques in integrated packages in order to produce phase diagrams from a minimum amount of empirical information and to compare with one another various approximate computational methods. These methods have been used to derive various binary alloy phase diagrams that agree remarkably well with those determined experimentally. The same theoretical techniques are being applied successfully to vacancy ordering in the high- T_c superconductors. It has also been proved that for some systems, and probably for many, inclusion of many-body effects beyond the mean-field or density-functional approximations should be taken carefully into account.

1. Determination of Effective-Pair Interactions in Random Alloys by Configurational Averaging (Publication 1)

H. Dreyssé,[†] A. Berera, L.T. Wille,[‡] and D. de Fontaine

A real-space method is presented for calculating effective-pair interactions (EPIs) in substitutionally disordered alloys, starting from electronic structure information for the constituting elements. The EPIs are obtained by averaging over a small number of randomly generated configurations. The electronic structure is calculated by tridiagonalizing a tight-binding Hamiltonian using the recursion method. Convergence, both as a function of the number of configurations and the number of

recursion levels, is rapid, and the results compare very well with other calculations. The advantage of the present scheme is that deviations from lattice periodicity can be taken into account in a completely straightforward way. The EPIs are essentially ingredients in statistical methods for determining alloy phase diagrams.

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2. Monte Carlo Study of Tracer and Chemical Diffusion of Oxygen in $\text{YBa}_2\text{Cu}_3\text{O}_{6+2c}$ (Publication 16)

E. Salomons and D. de Fontaine

Tracer and chemical diffusion of oxygen in $\text{YBa}_2\text{Cu}_3\text{O}_{6+2c}$ has been studied by Monte Carlo simulations of an asymmetric next-nearest-neighbor Ising model. Striking differences between tracer and chemical diffusion are found and explained by the effect of the thermodynamic factor, which is also determined by Monte Carlo simulation. Especially for $c = 0.5$, the effect of the thermodynamic factor is large. It is found that tracer diffusion in the ordered orthorhombic phase of $\text{YBa}_2\text{Cu}_3\text{O}_{6+2c}$ is strongly anisotropic, which is explained in terms of different diffusion mechanisms.

3. Low-Temperature Long-Range Oxygen Order in $\text{YBa}_2\text{Cu}_3\text{O}_z$ (Publication 18)

D. de Fontaine, G. Ceder, and M. Asta

Oxygen ordering in $\text{YBa}_2\text{Cu}_3\text{O}_z$ (YBCO) is responsible for the tetragonal-to-orthorhombic phase transition at high temperature and gives rise to additional ordered superstructures at low temperature. It is suggested here that such ordered superstructures are intimately related to the existence of "plateaus" in the T_c vs oxygen content observed by various investigators. The purpose of the present communication is to present a consistent theoretical model for oxygen ordering in YBCO featuring a parameter-free phase diagram for this system (see Figure 3-1) and an algorithm for determining additional ordered phases, the predicted structures and diffraction patterns of which agree closely with recent experimental findings.

*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Figure 3-1. Oxygen superstructure phase diagram of YBCO calculated with low-temperature cluster-variation-method algorithm. Input parameters from linear muffin-tin orbital calculations by P. Steme. Filled circles: experimental data from a Philips Research Laboratory preprint. Long-period oxygen superstructures are found between OI and OII phase regions. Phase separation is predicted, and observed, in the shaded region. (XBL 8910-6326)

4. Exactly Soluble Model for Antiphase Boundaries in Binary Ordering Alloys (Publication 6)

D.C. Chrzan and L.M. Falicov

An exactly soluble model that mimics the properties of {001} antiphase boundaries in the face-centered-cubic substitutional alloys (Ising antiferromagnets) with only nearest-neighbor interactions was developed. The three-dimensional model was extended to any dimension, including one- and two-dimensional systems. For three-dimensional systems, it was proven that, in the thermodynamic limit, antiphase boundaries are unstable at all temperatures. It was postulated that antiphase boundaries are unstable for all thermodynamic systems with dimension greater than one. In one dimension, where antiphase boundaries can be defined mathematically, the concentration of antiphase boundaries is 1/2 at both zero and infinite temperatures; but at all temperatures in between, the concentration is less than 1/2. Antiphase boundaries were found at equilibrium in higher-

dimensional systems with small sizes, the order of those used in Monte Carlo simulations of the Ising model. The implications of this unusual size effect were understood.

5. Work in Progress

The effect of impurities at the Cu(1) site in the basal plane of the high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{6+2c}$ on the oxygen-vacancy phase diagram is being investigated by Monte Carlo simulation of an asymmetric next-nearest-neighbor lattice gas model, in which the impurities are assumed to act as traps for oxygen atoms. First, the phase diagram of $\text{YBa}_2\text{Cu}_3\text{O}_{6+2c}$ is determined, which shows the high-temperature orthorhombic and antiorthorhombic phases. Next, the high-temperature orthorhombic-to-tetragonal transition of $\text{YBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{6+2c}$ is studied within a single orthorhombic domain. This is a true phase transition, with a peak in the specific heat, in contrast to the orthorhombic-to-pseudotetragonal transition studied in previous theoretical studies. The orthorhombic-to-tetragonal phase boundary is found to shift to higher oxygen concentrations with increasing impurity concentration. A first-order approximation for the shift of the phase boundary is derived that agrees with the Monte Carlo results.

The influence of magnetism in alloy behavior of the transition metals (iron, cobalt, and nickel) is being investigated with the hope of determining the influence on the magnetic properties of the local environment of an atom in an alloy.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. H. Dreyssé, A. Berera, L.T. Wille, and D. de Fontaine, "Determination of Effective Pair Interactions in Random Alloys by Configurational Averaging," *Phys. Rev. B* **39**, 2442 (1989); LBL-25659.
2. A. Berera and D. de Fontaine, "Oxygen-Vacancy Phase Equilibria in $\text{YBa}_2\text{Cu}_3\text{O}_x$ Calculated by the Cluster Variation Method," *Phys. Rev. B* **39**, 6727 (1989); LBL-25449.
3. D. de Fontaine, M.E. Mann, and G. Ceder, "States of Partial Order in $\text{YBa}_2\text{Cu}_3\text{O}_x$," *Phys. Rev. Lett.* **63**, 1300 (1989); LBL-27669.
4. M.L. Cohen and L.M. Falicov, "Magnon-Exchange Pairing and Superconductivity," *Science* **243**, 547 (1989); LBL-26089.
5. D.C. Chrzan and L.M. Falicov, "Theoretical Phase Stability of Incommensurate Spin Structures on the (001) Surfaces of MnO-Type Antiferromagnetic Semiconductors," *Phys. Rev. B* **39**, 3159 (1989); LBL-25875.

6. D.C. Chrzan and L.M. Falicov, "Exactly Soluble Model for Antiphase Boundaries in Binary Ordering Alloys," *Phys. Rev. B* **40**, 8194 (1989); LBL-26937.
7. L.M. Falicov, "Superconductivity, A Brief Introduction to Its Phenomenology and Theories," *IEEE J. Quantum Electron.* **25**, 2358 (1989); LBL-26756.

Other Publications

8. D. de Fontaine, "Electronic Structure and Phase Stability of Alloys," in *Materials Science Forum* **37**, 25 (1989), Proc. of U.S. Japan Seminar: "Electronic Structure and Lattice Defects in Alloys," May 4-7, 1987; LBL-24262.
9. D. de Fontaine, "The Cluster Variation Method and the Calculation of Alloy Phase Diagrams," in *Alloy Phase Stability*, G.M. Stocks and A. Gonis, Eds., Kluner Academic Publishers, Dordrecht, The Netherlands, 1989, p. 177; LBL-24934.
10. M. Sluiter, D. de Fontaine, X.Q. Guo, R. Podloucky, and A.J. Freeman, "Ab Initio Calculations of Ordered Intermetallic Phase Equilibria," in *MRS Proc. High Temperature Ordered Intermetallic Alloys III* **133**, 3 (1989); LBL-26727.
11. L.M. Falicov, "Superconductivity: Phenomenology," in *Proc. First Topsøe School on Superconductivity*, N.H. Andersen and K. Mortensen, Eds., Risø Publication M-2756 (Risø National Laboratory, Roskilde, Denmark), 1988, p. 7; LBL-25678.
12. L.M. Falicov, "1987: Open Problems in Condensed Matter Physics," in *Proc. Third Symp. Pan American Collaboration in Experimental Physics*, Rio de Janeiro, Brazil, Oct. 19-23, 1987, R. Rubinstein and A.F.S. Santoro, Eds., World Scientific, Singapore, 1989, p. 61; LBL-25687.

LBL Reports

13. D. de Fontaine, "States of Oxygen Ordering in $\text{YBa}_2\text{Cu}_3\text{O}_x$," International Centre for Theoretical Physics Conference on "Oxygen Disorder Effects in High T_c Superconductors," Trieste, Italy, Apr. 17-21, 1989; LBL-27267.
14. C.P. Burmester, M.E. Mann, G. Ceder, L.T. Wille, and D. de Fontaine, "Monte Carlo Simulation of Oxygen Ordering in $\text{YBa}_2\text{Cu}_3\text{O}_x$," *Physica C* (in press); LBL-28306.
15. G. Ceder, M. Asta, W.C. Carter, M.E. Mann, M. Kraitchman, and D. de Fontaine, "Phase Diagram and Low Temperature Behavior of Oxygen Ordering in $\text{YBa}_2\text{Cu}_3\text{O}_x$ Using *ab Initio* Interactions," *Phys. Rev. B* (in press); LBL-27970.
16. E. Salomons and D. de Fontaine, "Monte Carlo Study of Tracer and Chemical Diffusion of Oxygen in $\text{YBa}_2\text{Cu}_3\text{O}_{6+2x}$," *Phys. Rev. B* (in press); LBL-27971.
17. D. de Fontaine, "Critique of the Khachatryan and Morris Model for Oxygen Ordering in YBCO," LBL-27973.
18. D. de Fontaine, G. Ceder, and M. Asta, "Low Temperature Long-Range Oxygen Ordering in $\text{YBa}_2\text{Cu}_3\text{O}_x$," *Nature* (in press); LBL-27972.

19. D. de Fontaine, "Comment on Structural Properties of the Tetragonal Superconductors in $\text{LaBaCaCu}_3\text{O}_{7-x}$," *J. Less-Common Metals* (in press); LBL-28162.
20. G. Ceder, M. Asta, and D. de Fontaine, "Oxygen Ordering in $\text{YBa}_2\text{Cu}_3\text{O}_x$ at Low Temperature," *Mat. Res. Soc. Symp. Proc.: High Temperature Superconductors*, Nov. 26-Dec. 1, 1989 (in press); LBL-28163.
21. H. Dreyssé, G. Ceder, L.T. Wille, and D. de Fontaine, "Determination of Effective Pair Interactions and Segregation Behavior at Alloy Surfaces," *Vacuum* (in press); LBL-28307.
22. D.C. Chrzan, L.M. Falicov, J.M. MacLaren, X.-G. Zhang, and A. Gonis, "Magnetic Structure of {111} Stacking Faults in Nickel," submitted to *J. Appl. Phys.*; LBL-27781.
23. L.M. Falicov and D.C. Chrzan, "Incommensurable Surface Spin Structures in MnO-Type Antiferromagnets," LBL-27218.
24. L.M. Falicov, D.T. Pierce, S.D. Bader, R. Gronsky, K.B. Hathaway, H.J. Hopster, D.N. Lambeth, S.S.P. Parkin, G. Prinz, M. Salamon, I.K. Schuler, and R.H. Victora, "Surface, Interface, and Thin-Film Magnetism," LBL-27883.

Invited Talks

25. D. de Fontaine, "Pseudo-binary Phase Diagrams of the High- T_c Superconductor $\text{YBa}_2\text{Cu}_3\text{O}_x$," Los Alamos National Laboratory, Los Alamos, NM, Jan. 19, 1989.
26. D. de Fontaine, "Statistics of Vacancy Ordering in Superconductors," Mathematics Department, University of California at Berkeley, Mar. 17, 1989.
27. D. de Fontaine, "States of Oxygen Ordering in $\text{YBa}_2\text{Cu}_3\text{O}_x$," Conference on Oxygen Disorder Effects in High- T_c Superconductors, Trieste, Italy, Apr. 18-21, 1989.
28. D. de Fontaine, "Oxygen Ordering in $\text{YBa}_2\text{Cu}_3\text{O}_x$," IBM Thomas J. Watson Research Center, Yorktown Heights, NY, Apr. 24, 1989.
29. D. de Fontaine, "Thermodynamics of Oxygen Ordering in $\text{YBa}_2\text{Cu}_3\text{O}_x$," Department of Physics, RUCA, Antwerp, Belgium, May 23, 1989.
30. D. de Fontaine, "Pseudo-binary YBCO Phase Diagrams, a Comedy of Errors," CALPHAD XVIII, Saljöbaden, Sweden, May 28-June 2, 1989.
31. D. de Fontaine, "États d'ordre dans les supraconducteurs," Department of Materials Science, Université Catholique de Louvain, Louvain-la-Neuve, Belgium, June 5, 1989; Department of Physics, University of Nancy, France, June 7, 1989.
32. D. de Fontaine, "States of Oxygen Ordering in $\text{YBa}_2\text{Cu}_3\text{O}_x$," Institute for Studies in Interface Sciences, Physics Department, Facultés Universitaires Notre Dame de la Paix, Namur, Belgium, June 6, 1989.
33. D. de Fontaine, "Réactions d'ordre dans le supraconducteur $\text{YBa}_2\text{Cu}_3\text{O}_x$," Institut de Physique, Université Louis Pasteur, Strasbourg, France, June 9, 1989.

34. D. de Fontaine, "Calculation of Phase Diagrams from First Principles, Ti-Al Included," Wright-Patterson Air Force Base, Dayton, OH, Oct. 23, 1989.
35. D. de Fontaine, "Thermodynamics of Oxygen Vacancy Ordering in $\text{YBa}_2\text{Cu}_3\text{O}_x$ from First Principles," Joint Computational and Materials Sciences Seminar, University of Kentucky, Lexington, Oct. 24, 1989.
36. D. de Fontaine, "Oxygen Ordering in the Yttrium Compound Superconductors," MSME Department Seminar, University of California at Berkeley, Nov. 2, 1989.
37. L.M. Falicov, "Survey of Current Theories in High-Temperature Superconductivity," USDOE Information Meeting, Berkeley, CA, Jan. 27, 1989.
38. L.M. Falicov, "Theoretical Developments in High-Temperature Superconductivity," LBL Workshop, May 11, 1989.
39. L.M. Falicov, "Incommensurable Magnetic Surface Structures for MnO-Type Antiferromagnetic Insulators," 2nd International Workshop on the Magnetic Properties of Low-Dimensional Systems, San Luis Potosi, Mexico, May 23, 1989.
40. L.M. Falicov, "A Small-Cluster Approach to Highly Correlated Metals," IBM Almaden Research Center, San Jose, CA, Sept. 21, 1989.
41. L.M. Falicov, "The State of Condensed Matter Physics, 1989," Fourth Symposium on Pan-American Collaboration in Experimental Physics, Bariloche, Argentina, Nov. 7, 1989.
42. L.M. Falicov, "Superconductivity 1989: A Critical Review," Catholic University of Santiago, Chile, Nov. 14, 1989.
43. L.M. Falicov, "The Impact of Physics in the Understanding of the Contemporary World," Chilean Academy of Sciences and the Institute of Chile, in commemoration of the 25th Anniversary of the Institute of Chile, Santiago, Nov. 14, 1989.
44. D.C. Chrzan, "Magnetic Structure of [111] Stacking Faults in Nickel," Magnetism and Magnetic Materials Conference, Boston, MA, Nov. 28, 1989.

PHYSICAL PROPERTIES

High-Temperature Reactions*

Alan W. Searcy, Investigator

INTRODUCTION

The central purposes of this program are to develop models for important processes in materials science and to design and carry out critical experimental tests of the models. Theoretical studies under the program led to predictions that temperature gradients should significantly influence densification, creep, and solid-liquid transition temperatures. Experimental confirmation of these predictions has been obtained, and studies designed to clarify the role of temperature gradients on these processes are continuing. The conditions under which particles and pores develop facets during early and late stages of sintering are under experimental and theoretical study. Particular emphasis is placed on experiments with well-characterized nanometer-scale particles because of their potential for providing solids of superior properties and because they test the limits of some theoretical models

1. Transmission Electron Microscope Observation of Sintering by Nanometer-Scale Faceted MgO Particles (Publication 3)

M. Kim,[†] U. Dahmen, and A.W. Searcy

High-resolution transmission electron microscopy has been used to observe the changes in particle dimension when aligned 2-nm cross-section MgO particles within 1- μ m cross-section aggregates are sintered. Sintering in vacuum at 1500 K yields aligned particles with rectangular cross sections increased by a factor of 10 and porosities decreased to less than 20% of the initial value. The persistence of 2-nm surface features suggests that cooperative movement of the initial crystallites may

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contribute both to crystal growth and to densification within these aggregates (see Figure 1-1).

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2. The Influences of Temperature Gradients and Water Vapor on Creep of MgO Under Very Small Loads (Publication 6)

D. Beruto,[†] R. Botter,[‡] and A.W. Searcy

The possibility that temperature gradients might influence creep of low-relative-density ceramics had apparently never been investigated. Research completed this past year demonstrates that gradients of the order of 5 K/cm in low-density MgO compacts substantially increases creep over creep measured for isothermal compacts either in air or in water vapor (see Figure 2-1).

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Figure 1-1. MgO after sintering in vacuum for 1 hr at 1523 K of particles that were initially 2 nm in average cross section. (XBB 864-2935)

Figure 2-1. Variation of the melting point of tin with temperature gradients through the solid. Diamonds are from extrapolations in the solid, crosses are extrapolations in the liquid, and squares are from both. (XBL 898-2934)

3. Further Measurements of the Influence of Temperature Gradients on the Melting Point of Tin (Publication 4)

D. Beruto,[†] R. Botter,[‡] and A.W. Searcy

Last year steady-state temperature drops of 40 K through about 4 cm distances in solid tin were shown to reduce the melting temperature by 1.7 ± 0.8 K. The apparatus used in that study was modified to permit a steeper gradient, and the range of measurements was extended to investigate whether the melting-point depression was primarily a function of the temperature drop through varied lengths of solid or of the temperature gradient. New data over a wider range of gradients and temperature drops show clearly that the gradient is the major variable: when the gradient is 2.0 K/mm, the interface temperature is 3.8 ± 1.7 K below the normal melting point (see Figure 3-1).

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[‡]Permanent address: University of Genoa, Italy.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. D. Beruto, R. Botter, and A.W. Searcy, "The Influence of Temperature Gradients on Sintering: Experimental Tests of a Theory," *J. Am. Ceram. Soc.* **72**, 232 (1989); LBL-24197.

Figure 3-1. Percent axial strain under 10-KPa stress versus time. The temperature of isothermal hold or hold in a constant gradient was reached at about 20 minutes on the scale shown. Lowest curve run in vacuum at 1293 K; second curve in vacuum in a gradient from 1288 K to 1253 K; third in H₂O at 1288 K; fourth in H₂O at 1288 K to 1253 K. (XBL 898-2959)

2. M.G. Kim, M. Cima, and A.W. Searcy, "Comparison of Sizes of Magnesia Crystals Calculated from X-Ray Diffraction Line-Broadening and Transmission Electron Microscopy Observations," *J. Am. Ceram. Soc.* **72**, 1514 (1989); LBL-26391.

LBL Reports

3. M. Kim, U. Dahmen, and A.W. Searcy, "Transmission Electron Microscope Observation of Sintering by Nanometer Scale Faceted MgO Particles," LBL-28576.
4. D. Beruto, R. Botter, and A.W. Searcy, "Further Measurements of the Influence of Temperature Gradients on the Melting Point of Tin," LBL-28575.
5. A.W. Searcy, D. Beruto, and R. Botter, "How Temperature Gradients Can Influence Melting Points," symposium honoring Leo Brewer, Oct. 25, 1989; LBL-27761.
6. D. Beruto, R. Botter, and A.W. Searcy, "The Influences of a Temperature Gradient and Water Vapor on Creep of MgO Under Very Small Loads," LBL-28479.

Invited Talks

7. A.W. Searcy, "The Influence of Vacancies on the Stabilities of Crystalline Particles; Implications to Sintering," 91st Annual Meeting, American Ceramic Society, Indianapolis, IN, Apr. 24, 1989.
8. A.W. Searcy, "Chemical Considerations in High Temperature Composite Design," First International Ceramic Science and Technical Congress, Anaheim, CA, Nov. 3, 1989.

Ceramic Interfaces*

Andreas M. Glaeser, Investigator

INTRODUCTION

Numerous properties of ceramics depend strongly on microstructure, necessitating control of microstructural characteristics developed during processing. This research program focuses on improving our understanding of processes that dictate the microstructural changes occurring during processing and utilization. Microstructure development in model compacts formed from an "ideal," nominally monodispersed, chemically synthesized titania powder is being examined by applying transmission electron microscopy to ultramicrotomed sections of heat-treated compacts. The effects of crystallization, polymorphic phase transformations, and particle substructure on microstructural evolution are being studied. A broad range of model experiments utilizing photolithographically introduced, microdesigned intragranular or intergranular pore/flaw structures, illustrated in Figure 1-1, have been developed and applied

Figure 1-1. SEM micrographs of accessible surface structures: (a) monomodal arrays used for pore-boundary separation studies, (b) bimodal arrays for pore coarsening studies, (c) channel-like features for studying late-stage crack healing and Rayleigh instabilities, and (d) nonequilibrium shapes for studying facet development and surface energy anisotropy. (XBB 894-2696)

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to studies of the kinetics of interfacial processes. Phenomena amenable to study include pore-grain boundary separation, pore coarsening or elimination, faceting (surface energy anisotropy), and high-temperature crack healing. Future work will focus on further development and exploitation of this lithographic method.

1. High-Temperature Healing of Lithographically Introduced Cracks in Sapphire (Publication 2)

J. Rödel and A.M. Glaeser

A new technique for studying crack healing utilizing lithographically introduced cracklike defects has been developed. The effects of crack geometry, crystallography, microstructure, and chemistry can be studied more easily than with experimental methods used previously. The method has been applied to sapphire and used to study crack-healing behavior at 1800°C. Pronounced effects of crack-face crystallography on the healing mode have been demonstrated. Observations of cracks introduced at single crystal-polycrystal interfaces have identified grain-boundary grooving as a potential contributor to healing. Results suggest that inadvertently introduced contaminants can increase healing rates by several orders of magnitude (see Figure 1-2). Controlled localized introduction of the responsible impurities at surfaces could provide a means of facilitating low-temperature joining.

2. Anisotropy of Grain Growth in Alumina (Publication 3)

J. Rödel and A.M. Glaeser

Grain growth in theoretically dense undoped and MgO-doped alumina was studied, and average grain-boundary migration rates were compared to those of a-plane and c-plane sapphire during migration into the same undoped and MgO-doped materials. The results indicate a grain-size-dependent, grain-boundary-mobility-grain-boundary-energy product, $M_b\gamma_b$. More importantly, the grain-size dependencies of the $M_b\gamma_b$ products for seed and matrix grains differ. This may play an important role in initiating or sustaining abnormal grain growth. In addition, seed orientation appears to affect the nature of solute-boundary interactions. Although such boundary-misorientation-related differences have been demonstrated in metals, few, if any, equivalent studies have been performed in ceramics.

Figure 1-2. Effect of inadvertent contamination on healing rates of two otherwise identical cracks etched into the basal plane of sapphire. Crack evolution after (a) 0 min, (b) 5 min, and (c) 200 min at 1800°C. (XBB 883-2635)

3. Pore Drag and Pore-Boundary Separation in Alumina (Publication 4)

J. Rödel and A.M. Glaeser

Microdesigned interfacial pore structures were utilized to study pore drag and pore-boundary separation in alumina. This approach allowed the creation of pore arrays containing pores of controlled size and spacing at well-defined single-crystal seed/polycrystalline matrix interfaces, and enabled experimental determination of the peak pore velocity. From the peak pore velocity, a value of the surface diffusion coefficient pertinent to sintering was extracted. At 1600°C, the surface diffusion coefficient was $\approx 1 \times 10^{-7}$ cm²/sec for undoped alumina and $\approx 1 \times 10^{-7}$ cm²/sec for MgO-doped alumina. The values appeared to

be insensitive to the seed orientation for the two seed orientations studied. The results suggest a strong influence of pore spacing on the separation condition in undoped alumina, and a diminished influence in MgO-doped alumina. Good agreement between theoretical predictions of pore-boundary separation conditions and experimental observations was obtained. To our knowledge, we are the first to provide an experimentally determined "map" of pore-boundary separation conditions for a ceramic material. It is anticipated that this approach will be applicable to a broad range of ceramic materials and thus will provide a viable means of assessing the effects of dopant additions on pore-boundary separation conditions.

4. Work in Progress

Work exploring the effect of low-temperature heat treatment on microstructure development in nanoscale powder compacts should be concluded in 1991. Current efforts are focused on analyzing and quantifying the effects of lower-temperature processes such as crystallization to anatase, coarsening of anatase, transformation to rutile, and coarsening of rutile on densification and microstructure development during subsequent sintering at higher temperatures.

Completed work on high-temperature crack healing in sapphire has demonstrated that surface energy anisotropy, and thus crack-face and crack-edge crystallography, play an important role in dictating the healing behavior, even at temperatures that are a considerable fraction of the melting temperature. During the latter half of 1991, crack healing experiments on glass will be initiated. The high degree of control and reproducibility that can be exercised over the crack geometry should provide an ideal means of testing models describing crack healing in isotropic materials.

1989 PUBLICATIONS AND REPORTS

Other Publications

1. J. Rödel and A.M. Glaeser, "Photolithography: A New Tool for Ceramic Science," in *Processing Science of Advanced Ceramics*, I. Aksay and D.R. Ulrich, Eds., Mat. Res. Soc., Pittsburgh, PA, 1989, p. 293; LBL-27303.

LBL Reports

2. J. Rödel and A.M. Glaeser, "High-Temperature Healing of Lithographically Introduced Cracks in Sapphire," *J. Am. Ceram. Soc.* (in press); LBL-27197.

3. J. Rödel and A.M. Glaeser, "Anisotropy of Grain Growth in Alumina," submitted to J. Am. Ceram. Soc.; LBL-27360.
4. J. Rödel and A.M. Glaeser, "Pore Drag and Pore-Boundary Separation in Alumina," submitted to J. Am. Ceram. Soc.; LBL-27361.

Invited Talks

5. A.M. Glaeser, "Photolithography: A New Tool for Ceramic Science," International Symposium on Processing of Advanced Ceramics, Materials Research Society Spring Meeting, San Diego, CA, April 25-28, 1989.
6. A.M. Glaeser, "Joining Ceramics: An Overview," Lawrence Livermore National Laboratory, Livermore, CA, July 13, 1989.

SOLID-STATE PHYSICS

EXPERIMENTAL RESEARCH

Far-Infrared Spectroscopy*

Paul L. Richards, Investigator

INTRODUCTION

Improvements in infrared technology are making possible increases in the sensitivity of many types of infrared and millimeter wave measurements. In this project, improved types of infrared sources, spectrometers, and detectors are being developed. Also, improved infrared techniques are being used to do experiments in areas of fundamental and applied infrared physics where their impact is expected to be large. Experiments in progress include measurements of the far-infrared absorptivity of one-dimensional conductors, and measurements of the heat capacity of monolayers of adsorbates on metal films. Improvements in infrared technology include development of thin-film high- T_c superconducting bolometers for detecting x-ray, infrared, and microwave radiation; development of superconducting thin-film quasiparticle detectors and mixers for near-millimeter wavelengths that approach quantum-limited sensitivity; and development of a new source for broadly tuned far-infrared spectroscopy based on harmonic generation from microwave oscillators.

1. AC Calorimeter for Measurements of Adsorbed Gases on Metal Films at ^4He Temperatures (Publications 19 and 22)

T.W. Kenny,[†] R.B. Phelps, and P.L. Richards

An analysis is presented of the performance of an ideal ac calorimeter limited only by thermodynamic noise. A calorimeter based on this analysis and designed for studies of the heat capacity of atomic and molecular adsorbates is described. This novel ac calorimeter is the first instrument capable of measuring the heat capacity of adsorbed gases on high-quality, well-characterized metallic substrates.

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Since the corrugation in the physisorption potential of metals is generally smaller than that of other materials (such as exfoliated graphite) typically used as substrates in such studies, this new ac calorimeter improves the prospects for observing true two-dimensional behavior.

A schematic diagram of the calorimeter is shown in Figure 1-1. The calorimeter consists of a Ge:Ga thermometer and NiCr heaters mounted on one side of a sapphire substrate. The calorimeter is mounted on a ^4He cold finger in a UHV system, and a metal film is deposited *in situ* on the opposite side. The metal film is then exposed to a flux of molecules from an effusion cell. The heat capacity of the calorimeter is measured as a function of temperature both before and after the dose, and subtraction of the two curves yields the heat capacity of the adsorbate. The coverage of the surface cannot be measured independently, but in some cases it may be extracted from the heat-capacity data. In such cases, sticking coefficients may also be deduced, since the number of molecules incident on the calorimeter is known.

In order to verify the performance of the calorimeter, measurements have been made of the heat capacity of 25- μm samples of indium, and of submonolayer coverages of ^4He on sapphire. The discontinuity in the heat capacity due to the superconducting transition in an indium sample is

Figure 1-1. Schematic drawing of the calorimeter. The Ge:Ga thermometer, NiCr heaters, and Cu wires are attached to the back of the sapphire substrate with conductive epoxy. Ag films are deposited *in situ* on the front of the sapphire. (XBL 893-5074)

shown in Figure 1-2. The measured sensitivity of the calorimeter corresponds to $<10^{-2}$ monolayers of ^4He adsorbed on the surface of the calorimeter in the gas phase.

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2. Heat-Capacity and Sticking-Probability Measurements of the ^4He Submonolayers Adsorbed on Evaporated Ag Films—Bose Statistics in Two Dimensions (Publication 23)

T.W. Kenny,[†] R.B. Phelps, and P.L. Richards

We have used a novel ac microcalorimeter to measure the heat capacity of submonolayers of ^4He adsorbed on Ag films between 1.7 and 3.3 K. Good fits to the results are obtained with a model of a noninteracting two-dimensional Bose gas. This is the first observation of the Bose gas in experimental studies of adsorbed monolayers.

The heat-capacity data for several coverages of ^4He are shown as a function of temperature in Figure 2-1. The lines through the data give the heat capacity computed for a noninteracting 2D Bose gas of ^4He atoms for the coverages shown on the right-hand side of the graph. Since the number of atoms incident on the Ag surface is known from the geometry of our dosing apparatus, these coverages can be used to derive sticking coefficients for room-temperature ^4He atoms incident on cold Ag. The sticking probability is 4% at low coverage, and abruptly drops to 1% for coverages above 0.5 monolayers.

Figure 1-2. Heat capacity as a function of temperature for a 25- μm sample of indium attached to the calorimeter with conductive epoxy. The discontinuity in the heat capacity is due to the superconducting transition of the indium. (NBL 8810-7634)

The results shown in Figure 2-1 are in sharp contrast with those observed in the ^4He /graphite system. In the latter system, Schottky-type anomalies and melting peaks cause the heat capacity to deviate upward at low temperature. This difference in the temperature dependence demonstrates that the substrate has a significant effect on the behavior of the adsorbed ^4He , and it underscores the importance of the new ac microcalorimeter as a means of expanding the domain of available substrates. Any metal that can be evaporated in UHV may be used as a substrate in this apparatus. Future plans include experiments with ^4He on gold. Since the binding energy of ^4He on Au is intermediate between that of ^4He /graphite and ^4He /Ag, such an experiment will be important in identifying effects due to the substrate.

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3. Observation of Nondissipative Quasiparticle Tunnel Currents in Superconducting Tunnel Junctions (Publication 24)[†]

Q. Hu,[‡] C.A. Mears, and P.L. Richards

We have demonstrated for the first time the existence of nondissipative quasiparticle tunneling between two superconductors. Superconducting tunnel junctions carry tunneling currents due both to electron pairs (Cooper pairs) and to single electrons (quasiparticles) excited above the superconducting ground state. The tunneling current for

Figure 2-1. Measurements of the temperature dependence of the heat capacity for a series of coverages of ^4He on Ag films. The solid lines correspond to the calculated heat capacity of a two-dimensional noninteracting Bose gas. (XBL 893-5067)

each type exhibits both resistive (in-phase) and reactive (out-of-phase) response to an oscillatory drive. For Cooper pairs, the in-phase component is the Josephson $\cos \phi$ term, and the out-of-phase component is the Josephson $\sin \phi$ term. For quasiparticles, the resistive, or dissipative, term is due to real photon-assisted tunneling events, while the out-of-phase, nondissipative term is due to the "sloshing back and fourth" of quasiparticles caused by the absorption and subsequent re-emission of photons.

Quasiparticle resistive tunneling and the Josephson $\sin \phi$ term are easy to measure and have been studied extensively since the 1960s. Many attempts to measure the Josephson $\cos \phi$ term were published in the late 1970s, but the results remain ambiguous. In this work, the quasiparticle reactive currents were measured for the first time.

The quasiparticle reactive current manifests itself as an excess reactance of the superconducting tunnel junction that depends on bias voltage. This reactance was precisely measured by placing the junction in a millimeter-wave resonant circuit and measuring the change in resonant frequency of the circuit when the bias voltage across the junction was changed. Figure 3-1(a) shows the measured and calculated values of the resonant frequency as a function of bias voltage. The solid line is the theoretical prediction with the quasiparticle reactive currents included, and is in excellent agreement with the experimental points. The dashed line is the theoretical prediction when the effect of the quasiparticle reactive current is not included. Figure 3-1(b) shows the linewidth of this resonance as a function of bias voltage. The dots are the experimental results, and the solid line is the theoretical prediction.

The quasiparticle reactive current plays a subtle but important role in the performance of high-frequency superconducting detectors and mixers. The dependence of this current on applied bias voltage suggests applications to voltage-tunable circuits in the millimeter-wave band. Analogous effects should play a similar role in other types of high-frequency devices, including semiconducting quantum-well transistors, mixers, harmonic generators, and oscillators that are currently under development.

Figure 3-1. (a) Resonant frequency of a circuit containing a superconducting tunnel junction as a function of dc bias voltage. The dots are the experimentally measured results; the solid line is calculated from the Werthamer-Tucker theory; the dashed line is the calculated result without including the quasiparticle reactive current. (b) Linewidth of the resonance as a function of dc bias voltage. The dots are the experimental results, and the solid line is calculated from theory. (XBL 8911-5261)

4. Quantum-Limited Heterodyne Detection of mm Waves using Superconducting Tantalum Tunnel Junctions (Publication 19)

C.A. Mears, Q. Hu,[†] P.L. Richards, A. Worsham, D.E. Prober, and A.V. Raisanen

Quasiparticle superconductor-insulator-superconductor (SIS) mixers have been shown to be the lowest-noise coherent receivers over the millimeter and submillimeter range of the electromagnetic spectrum. However, even the best of these receivers have fallen short of the performance predicted by Tucker's theory of quantum mixing. Because

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of the lack of detailed comparisons between experimental and theoretical performance, it has been unclear whether discrepancy between actual performance and predicted performance is due to difficulties in coupling the signal to the mixer, or to flaws in the Tucker theory.

In order to understand the cause for these discrepancies, we have made an accurate measurement of the mixer noise and mixer gain of SIS mixers employing small-area (1 mm^2) Ta/Ta₂O₅/Pb_{0.9}Bi_{0.1} tunnel junctions. These junctions have very low subgap leakage current and an extremely sharp current rise at the sum-gap. These features make them ideal for testing mixer theory in the quantum limit. We have measured the performance of an SIS mixer operating in the limit where the noise is limited by the uncertainty principle. The added mixer noise was 0.61 ± 0.31 quanta at 95.0 GHz, which is within a factor 1.3 of the quantum limit of 0.5 quanta. This is the closest approach to the quantum limit measured in any SIS mixer.

To compare our results with the Tucker theory, it is necessary to determine the imbedding admittances seen by the mixer at the upper and lower sideband frequencies. We deduced a range of these admittances consistent with the shapes of I-V curves pumped at the upper and lower sideband frequencies. Using these admittances, the mixer performance predicted by quantum theory is in good agreement with experiment. In Figure 4-1, we plot experimentally measured values of the mixer noise and gain as a function of local oscillator power, and compare them with the theoretically predicted range of performance.

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5. Design Analysis of a High- T_c Superconducting Microbolometer (Publication 8)

Q. Hu,[†] M. Nahum, and P.L. Richards

We propose an antenna-coupled microbolometer based on the resistive transition of a high- T_c superconducting film as a detector for far-infrared and millimeter waves. Such microbolometers can be mechanically stronger, more easily fabricated, and much faster than conventional bolometric infrared detectors. A design analysis shows that a noise equivalent power of $2.5 \times 10^{-12} \text{ W Hz}^{-1/2}$ is achievable for modulation frequencies up to 100 kHz. The superconducting film must be of high quality with narrow resistive transition and low $1/f$ noise.

We have fabricated and tested the performance of several high- T_c microbolometers. A typical configuration consists of a small ($\approx 5 \times 5 \text{ } \mu\text{m}^2$) area of a high- T_c film deposited onto a thick substrate. A planar lithographed

Figure 4-1. Mixer noise and mixer gain plotted as a function of local oscillator power. The squares are the experimental points, and the area between the dotted lines is the range of performance consistent with an IV curve shape. The solid line, which is in near perfect agreement, is the performance predicted for one specific set of upper and lower sideband admittances. (XBL 901-5398)

antenna is used to couple the radiation to the superconductor. The optical efficiency is further enhanced by mounting the substrate on the flat side of a dielectric lens. Due to its small size, both the thermal conductivity of the film into the bulk of the substrate and the heat capacity of the thermally active region are small. Consequently, the microbolometer is expected to have low noise, fast response, and a high voltage responsivity. The measured speed of prototype devices is in good agreement with this prediction (see Figure 5-1).

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6. Work in Progress

Direct bolometric absorptivity measurements of high- T_c superconductors have been perfected to provide high accuracy over a wide far-infrared spectral range, from ~ 3 to

Figure 5-1. Measured (at 90 GHz) and calculated responsivities of a typical microbolometer normalized at zero frequency. (XBL 8911-5254)

1200 cm^{-1} . The accuracy is being checked by measuring both normal and low- T_c superconducting metals whose absorptivity is known. Systematic measurements on films from a variety of sources is in progress.

Conventional bolometric infrared detectors are being fabricated and tested that use the resistive transition of a high-temperature superconductor as a sensitive thermometer. The thin films of c-axis $\text{YBa}_2\text{Cu}_3\text{O}_7$ are deposited at Conductus, Inc., by single-target sputtering on 25- μm -thick sapphire substrates. Sapphire is used for its mechanical strength and low heat capacity. The substrates are then diced into $1 \times 1 \text{ mm}^2$ bolometer chips. A low noise readout is achieved by patterning the film into a meander line to obtain a bolometer resistance $\leq 500 \Omega$ and making electrical contact with evaporated silver. The best performance achieved is a noise-equivalent power (NEP) of $5 \times 10^{-9} \text{ W Hz}^{-1/2}$ for an optical signal chopped at 20 Hz. Calculations indicate the NEP can be reduced to $10^{-11} \text{ W Hz}^{-1/2}$ with expected improvements in YBCO film quality. If such performance is attained, high- T_c bolometers will be especially useful as infrared detectors of wavelengths longer than the $\sim 20\text{-}\mu\text{m}$ cutoff of liquid-nitrogen-cooled photovoltaic detectors. Potential applications include far-infrared laboratory spectrometers and passively cooled space observations of bright sources.

The microcalorimeter constructed to measure the heat capacity of physisorbed submonolayers on metal surfaces is being used to measure ortho- and para-hydrogen on a silver substrate.

The search for the far-infrared optical phason mode in the charge-density-wave compounds TaS_3 and $\text{K}_{0.3}\text{MoO}_3$ is nearing completion.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. C.A. Mears, Q. Hu, and P.L. Richards, "Numerical Simulation of Experimental Data from Planar SIS Mixers with Integrated Tuning Elements," *IEEE Trans. Magn.* **MAG-25**, 1050 (1989); LBL-25813.[†]
2. Q. Hu, C.A. Mears, P.L. Richards, and F.L. Lloyd, "MM Wave Quasioptical SIS Mixers," *IEEE Trans. Magn.* **MAG-25**, 1380 (1989); LBL-25814.[†]
3. P.L. Richards, S. Verghese, T.H. Geballe, and S.R. Spielman, "The High T_c Superconducting Bolometer," *IEEE Trans. Magn.* **MAG-25**, 1335 (1989); LBL-25812.[‡]
4. T.W. Kenny, P.L. Richards, I.S. Park, E.E. Haller, and J. Beeman, "Bias Induced Nonlinearities in Neutron Transmutation Doped Germanium at ^4He Temperatures," *Phys. Rev. B* **39**, 8476 (1989); LBL-25633.
5. G.M. Bernstein, M.L. Fischer, P.L. Richards, J.B. Peterson, and T. Timusk, "Anisotropy of the Diffuse Background at Millimeter Wavelengths," *Astrophys. J. Lett.* **337**, L1 (1989).[¶]
6. P.L. Richards, J. Clarke, R. Leoni, P. Lerch, S. Verghese, M.R. Beasley, T.H. Geballe, R.H. Hammond, P. Rosenthal, and S.R. Spielman, "Feasibility of the High T_c Superconducting Bolometer," *Appl. Phys. Lett.* **54**, 283 (1989); LBL-26113.[‡]
7. P.L. Richards and Q. Hu, "Superconducting Components for Infrared and Millimeter Wave Receivers," *Proc. IEEE* **77**, 1233 (1989); LBL-26169.[†]
8. Q. Hu and P.L. Richards, "Design Analysis of a High T_c Superconducting Microbolometer," *Appl. Phys. Lett.* **55**, 2444 (1989); LBL-27645.[‡]

Other Publications

9. T. Matsumoto, S. Hayakawa, H. Mutsuo, H. Murakami, S. Sato, A.E. Lange, and P.L. Richards, "Cosmic Background Radiation in the Submillimeter Range," in *Proc. Yamada Conf. XX on Big Bang, Active Galactic Nuclei & Supernovae*, Universal Academy Press, Inc., Tokyo, Japan, 1989, p. 213.^{¶**}
10. P.T. Timbie, G.M. Bernstein, and P.L. Richards, "An Adiabatic Demagnetization Refrigerator for SIRTf," *IEEE Trans. Nucl. Sci.* **36**, 898 (1989).[¶]
11. G.M. Bernstein, M.L. Fischer, P.L. Richards, J.B. Peterson, and T. Timusk, "New Measurements of the Anisotropy and Spectrum of the Millimeter Wave Background," in *Proc. Workshop on Particle Astrophysics: Forefront Experimental Issues*, E.B. Norman, Ed., World Sci. Publ. Co., Singapore, 1989, p. 123.[¶]
12. G.M. Bernstein (Ph.D. Thesis), "Measurements of the Spectrum and Anisotropy of the Millimeter Wave Background."[¶]

13. G.M. Bernstein, P.T. Timbie, and P.L. Richards, "A 100 mK Bolometer System for SIRTf," in *Proc. Third Infrared Detector Technology Workshop*, NASA Technical Memorandum 102209, Oct. 1989, p. 35.[†]
14. P.L. Richards and Q. Hu, "Progress in Superconducting Mixers and Detectors for Infrared and Millimeter Waves," in *Extended Abstracts of ISEC'89*, 1989, p. 46; LBL-27223abs.[†]
15. P.L. Richards, "High T_c Superconducting Infrared Detectors," in *Extended Abstracts of the 6th International Workshop on Further Electron Devices; 2nd Workshop on High-Temperature Superconducting Electron Devices*, 1989, p. 391; LBL-27224abs.[†]
16. J.W. Beeman, E.E. Haller, W.L. Hansen, P.N. Luke, and P.L. Richards, "Stressed Ge:Ga Photoconductors for Space-Based Astronomy," in *Proc. Third Infrared Detector Technology Workshop*, NASA Technical Memorandum 102209, 1989, p. 5.[†]
17. C.A. Mears, Q. Hu, P.L. Richards, A. Worsham, and D. Prober, "SIS Quasiparticle Heterodyne Mixers Using Tantalum Junctions," *Bull. Am. Phys. Soc.* **34**, 695 (1989); LBL-26398abs.[†]
18. T.W. Kenny and P.L. Richards, "Heat Capacity Measurements of ^4He Submonolayer Films Adsorbed on Sapphire," *Bull. Am. Phys. Soc.* **34**, 818 (1989); LBL-26398abs.
19. D. Miller, T.W. Kenny, P.L. Richards, S.R. Spielman, and T.H. Geballe, "Infrared Absorptivity Measurement on Thin Film ErBaCuO ," *Bull. Am. Phys. Soc.* **34**, 792 (1989); LBL-24504abs.
26. P.L. Richards, "Astrophysics," Symposium on Frontiers of Applied Physics, Stanford University, Stanford, CA, Jan. 21, 1989.
27. P.L. Richards, "The High- T_c Superconducting Bolometer," Seventh DOE/BES/DMS Information Meeting on High- T_c Superconductivity, LBL, Jan. 27, 1989.
28. P.L. Richards, "Background Astronomy at Millimeter and Submillimeter Wavelengths," All Moscow Cosmology Colloquium, Moscow State University, Moscow, U.S.S.R., Feb. 20, 1989; Space Research Institute of the Soviet Academy of Science, Moscow, U.S.S.R., Feb. 22, 1989.
29. P.L. Richards, "Infrared Divergence in the Cosmic Microwave Background," Department of Applied Science Colloquium, University of California, Davis, Livermore, CA, Mar. 7, 1989.
30. P.L. Richards, "Potential Collaborations with the Soviet Union, NASA Management Operations Working Group for Infrared Millimeter Wave and Radio Astronomy," Goddard Space Flight Center, Greenbelt, MD, Mar. 10, 1989.
31. P.L. Richards, "High- T_c Materials and Applications," High- T_c Spring 1989 Workshop, MCSO, LBL, May 11, 1989.
32. P.L. Richards, "Submillimeter Background Astronomy: A New Window on the Early Universe," Physics Department, University of California, Santa Barbara, May 23, 1989.
33. P.L. Richards, "High T_c Superconducting Infrared Detectors," 6th International Workshop on Future Electron Devices, 2nd Workshop on High-Temperature Superconducting Electron Devices, Hokkaido, Japan, June 7-9, 1989.
34. P.L. Richards, "Progress in Superconducting Mixers and Detectors for Infrared and Millimeter Waves," 1989 International Superconductivity Electronics Conference, ISEC'89, Tokyo, Japan, June 12-13, 1989.
35. P.L. Richards, "Spectrum of the Microwave Background," The Microwave Background 25 Years Later, l'Aquila, Italy, June 19-23, 1989.
36. P.L. Richards, "Bolometric Infrared Sensors: Non-Superconducting and Superconducting," 1989 Superconducting Electronics Workshop, St. Michaels, MD, Oct. 1-5, 1989.
37. P.L. Richards, "High T_c Applications: Infrared and Millimeter Wave Sensors," American Vacuum Society 36th National Symposium and Topical Conference, Boston, MA, Oct. 23, 1989.
38. P.L. Richards, "Adiabatic Demagnetization Refrigerator," NASA Workshop on Submillimeter Astronomy, California Institute of Technology, Pasadena, CA, Oct. 30, 1989.
39. Q. Hu, "Quantum-Limited Microwave and Infrared Detection Using Superconducting Devices," Department of Physics, University of California, Los Angeles, Jan. 18, 1989; Department of Physics, Brown University, Providence, RI, Mar. 7, 1989; Division of Applied Physics, Yale University, New Haven, CT, Mar. 9, 1989.
40. Q. Hu, "Superconducting Components for Infrared and Millimeter Wave Receivers," High T_c Superconductivity Consortium Symposium, University of California, Los Angeles, Mar. 10, 1989.

LBL Reports

20. T.W. Kenny (Ph.D. Thesis), "Heat Capacity Measurements on Atoms and Molecules Adsorbed on Evaporated Metal Films," LBL-27265.
21. Q. Hu and P.L. Richards, "Quasiparticle Mixers and Detectors," chapter in *Modern Superconducting Devices*, Academic Press, Boston (in press); LBL-26535.[†]
22. T.W. Kenny and P.L. Richards, "AC Calorimeter for Measurements of Adsorbed Gases on Metal Films at ^4He Temperatures," *Rev. Sci. Instrum.* (in press); LBL-27508.
23. T.W. Kenny and P.L. Richards, "Heat Capacity and Sticking Probability Measurements of ^4He Adsorbed on Evaporated Ag Films—Bose Statistics in Two Dimensions," submitted to *Phys. Rev. Lett.*; LBL-27509.
24. Q. Hu, C.A. Mears, P.L. Richards, and F.L. Lloyd, "Observation of Non-Dissipative Quasiparticle Tunnel Currents in Superconducting Tunnel Junctions," submitted to *Phys. Rev. Lett.*; LBL-28284.[†]

Invited Talks

25. P.L. Richards, "Single-Particle Tunneling SIS Mixers, Superconductors and Their Applications," University of California, San Francisco, Jan. 10, 1989.

41. Q. Hu, "Quantum-Limited Millimeter Wave Detection Using Superconducting Devices," EECS Department, Massachusetts Institute of Technology, Cambridge, MA, Apr. 18, 1989.
42. Q. Hu, "Superconducting Bolometric Detectors," EECS Department, University of California at Berkeley, Dec. 4, 1989.
43. Q. Hu, "Observation of Quantum Susceptance in Superconducting Tunnel Junctions," National Institute of Standards and Technology, Boulder, CO, Dec. 21, 1989.
44. Q. Hu, "A High T_c Superconducting Bolometer," National Institute of Standards and Technology, Boulder, CO, Dec. 22, 1989.
45. P.T. Timbie, "Millimeter Wave and Far Infrared Detectors for Astrophysics," Department of Electrical Engineering, University of Michigan, Ann Arbor, Feb. 1, 1989.
46. P.T. Timbie, "Searches for Anisotropy in the Cosmic Microwave Background Radiation," Department of Physics, Brown University, Providence, RI, Apr. 24, 1989; Harvard University Center for Astrophysics, Cambridge, MA, May 1, 1989.
47. P.T. Timbie, "Development of an Adiabatic Demagnetization Refrigerator for SIRTf," 1989 Space Cryogenics Workshop, California Institute of Technology, Pasadena, CA, July 31-Aug. 1, 1989.
48. P.T. Timbie, "100 mK Bolometers for the Submillimeter Explorer," 1989 NASA/CNES Submillimeter Workshop, California Institute of Technology, Pasadena, CA, July 31-Aug. 2, 1989.
49. P.T. Timbie, "Astronomical Applications of Far-Infrared Detectors," Ford Aerospace, Greenbelt, MD, Dec. 4, 1989.

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Experimental Solid-State Physics and Quantum Electronics*

Y.R. Shen, Investigator

INTRODUCTION

The general objective of this program is to study laser interaction with matter and to apply laser techniques to studies of materials. Work is being carried out in both theory and experiment. In recent years, second-order nonlinear optical processes have been developed as effective surface probes under this program. Current projects are focused on applications of such techniques to studies of transition-metal surfaces in ultrahigh vacuum. Second-harmonic generation can be used to probe molecular adsorption and desorption from a metal surface, to study laser thermal desorption, to monitor the formation and disappearance of monolayer grating, and to measure surface diffusion of molecules. The possibility of using second-harmonic generation to probe surface magnetization has also been considered.

1. Laser-Induced Thermal Desorption of CO on Ni(111); Determination of Pre-Exponential Factor and Heat of Desorption (Publication 2)

X.D. Zhu, Th. Rasing, and Y.R. Shen

Molecular adsorption and desorption are subjects of great importance in modern surface science, as they provide information on the binding energy of adsorbates, states of adsorption, and nature of adsorbate-substrate and adsorbate-adsorbate interactions. Desorption is governed by the activation energy E_d and the pre-exponential factor ν . The former describes the energy required for a molecule to desorb, while the latter is related to the state (mobile or immobile) the adsorbates are in prior to desorption. Experimental determination of E_d and ν and their dependences on the surface coverage in comparison with theory will therefore allow a better understanding of an adsorbate-substrate system. Conventional thermal-desorption spectroscopy (TDS) is often used to deduce E_d and ν . It has, however, been recognized that a separate determination of E_d and ν with good accuracy requires a very careful execution of the experiment. Measurements of

the number of desorbed molecules must be highly accurate and free of background noise. We show that by combining laser-induced thermal desorption with conventional thermal-desorption spectroscopy, one can determine separately the activation energy E_d and the pre-exponential factor ν for desorption with good accuracy. Results on CO on Ni(111) yield $E_d \approx 25.5$ kcal/mol and $\tau \approx 10^{13}$ /sec (see Figure 1-1). They agree well with values obtained by other techniques and suggest that, above room temperature, CO on Ni(111) is a highly mobile gas-like phase.

2. Generation and Detection of a Monolayer Grating by Laser Desorption and Second-Harmonic Generation: CO on Ni(111) (Publication 5)

X.D. Zhu and Y.R. Shen

Laser-induced dynamic gratings have found many important applications in modern science and technology. They range from phase conjugation for real-time image reconstruction to material studies. In the latter case, monitoring of the time-dependent relaxation of the dynamic gratings in a medium allows us to deduce useful information on the dynamic properties that govern the diffusion of particles, energy, and even phases of coherent excitations in the medium. So far, research in this area has been heavily concentrated on bulk samples. It may seem obvious that the same scheme should be applicable to surfaces or interfaces to yield similar information on the surface dynamic properties. However, a surface grating one

Figure 1-1. Experimental laser-induced thermal desorption (LITD) data (open circles), together with theoretical predictions. Dotted line: $\nu \approx 10^{16}$ /sec and $E_d \approx 32.9$ kcal/mol. Dashed line: $\nu \approx 10^{13}$ /sec and $E_d \approx 25.5$ kcal/mol. Solid curve corresponds to $\nu \approx 0.91 (k_B T/h) \theta$ and $E_d = E_d(0) - 3/2 RT$.¹ (XBL 883-7319)

*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

1. H. Pfnur, P. Feulner, H.A. Engelhardt, and D. Menzel. Chem. Phys. Lett. **59**, 481 (1978).

or several monolayers thick is often difficult to monitor. This is particularly true for gratings composed of monolayers of small molecules. Diffraction of a probe beam by such a grating is easily masked by scattering of the beam from the bulk.

Recently optical second-harmonic generation (SHG) has been demonstrated to be highly surface specific. It can therefore be an ideal method to probe surface monolayer gratings. Here we report the first study of controlled generation of monolayer gratings of CO on Ni(111) by laser-induced desorption and the subsequent detection of the gratings by SHG. The experimental arrangement is shown in Figure 2-1.

For the generation of a CO monolayer on the Ni(111) sample, we used the technique of laser desorption by interfering two 1.06- μm laser beams on the sample covered by a CO monolayer. The grating was then probed by surface SHG using a 0.53- μm probe beam. Four orders of diffraction were observed. The experimental results are in very good agreement with theoretical predictions (see Figure 2-2).

3. Surface Diffusion of CO on Ni(111) Studied by Diffraction of Optical Second-Harmonic Generation off a Monolayer Grating (Publication 1)

X.D. Zhu, Th. Rasing, and Y.R. Shen

Surface diffusion is a subject of great importance in modern science. It often plays a major role in limiting a surface reaction. While molecular adsorption and desorption probe the potential variation perpendicular to the surface, surface diffusion probes the potential variation in the surface. Adsorbate-adsorbate and adsorbate-substrate interactions are expected to have different effects on desorption and on surface diffusion. The classical and

Figure 2-1. Schematic of the experimental arrangement for generation and characterization of the monolayer grating of CO on Ni(111) in ultrahigh vacuum. (XBL 8810-7614)

Figure 2-2. Measured (unshaded) and calculated (shaded) square roots of various orders of diffraction from the monolayer grating of CO on Ni(111). (XBL 8810-7615)

quantum natures of surface diffusion have also attracted much attention. Despite the tremendous interest in the process, research in this area is still rather limited because of the lack of convenient tools.

We introduce here a laser-induced surface grating technique to study surface diffusion. In our technique, two pulsed laser beams intersecting on the surface under investigation are used to burn a grating by thermal desorption of an adsorbed molecular monolayer (see Figure 2-1). Subsequently, diffraction of surface optical SHG from the grating is used to detect the smearing of the grating due to surface diffusion of the adsorbed molecules. We have applied the technique to CO on Ni(111) in ultrahigh vacuum. The preliminary results (see Figure 3-1) allow us to deduce a diffusion energy $E_{\text{diff}} \approx 6.9$ kcal/mole with a pre-exponential factor $D_0 \approx 1.2 \times 10^{-5}$ cm²/sec.

4. Optical Second-Harmonic Generation from Magnetized Surfaces (Publication 3)

R-P. Pan, H.D. Wei, and Y.R. Shen

The controversy over the observation of magnetically "dead" layers almost two decades ago has sparked continuing intensive studies in the field of surface magnetism. From the basic research point of view, the fact that the surface and the bulk of the same material can have very different magnetic properties is certainly most interesting and intriguing. Improved understanding of the role of surfaces in magnetic phase transitions will also help

Figure 3-1. Normalized first-order diffracted SHG as functions of time at various sample temperatures after laser desorption. Solid circles: $T = 219$ K; open triangles: $T = 247$ K; solid squares: $T = 261$ K; open circles: $T = 273$ K. The solid curves are least-square fits using single exponential functions with the exponent $\alpha = 2\pi^2 D(T)/a^2$ as the adjustable parameter. (XBL 887-7488)

shed light on other physical phenomena such as surface melting. From the application point of view, the fact that magnetic memory devices could be affected by surface magnetization naturally calls for a better understanding of surface magnetism. The surface magnetic properties of transition metals are also of pivotal importance for catalysis and metallurgy.

Experimental studies in this field have, however, been impeded by the limited number of analytical tools available. We propose optical SHG as a means to probe surface magnetization. It is shown that surface magnetization can induce a number of nonlinear susceptibility elements that would vanish otherwise. They are presented for the (001), (110), and (111) surfaces of a fcc centrosymmetric crystal. An order-of-magnitude estimate, using the microscopic expression of the nonlinear susceptibility, suggests that these induced elements are detectable by optical SHG with appropriate polarization combinations. The second-harmonic signals from magnetized and nonmagnetized surfaces should exhibit characteristically different rotational anisotropy.

5. Work in Progress

SHG is being used to probe CO adsorption and desorption on Ni(110). Preliminary results show that the behavior is very different from that of CO on Ni(111). The same technique is also being employed to study anisotropy in the surface diffusion of CO on Ni(111).

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. X.D. Zhu, Th. Rasing, and Y.R. Shen, "Surface Diffusion of CO on Ni(111) Studied by Diffraction of Optical Second-Harmonic Generation off a Monolayer Grating," *Phys. Rev. Lett.* **61**, 2883 (1988); LBL-25970.
2. X.D. Zhu, Th. Rasing, and Y.R. Shen, "Laser-Induced Thermal Desorption of CO on Ni(111): Determination of Pre-exponential Factor and Heat of Desorption," *Chem. Phys. Lett.* **155**, 459 (1989); LBL-25189.
3. R-P. Pan, H.D. Wei, and Y.R. Shen, "Optical Second Harmonic Generation from Magnetized Surfaces," *Phys. Rev. B* **39**, 1229 (1989); LBL-26093.
4. Y.R. Shen, "Surface Properties Probed by Second-Harmonic and Sum-Frequency Generation," *Nature* **337**, 519 (1989); LBL-26099.
5. X.D. Zhu and Y.R. Shen, "Generation and Detection of a Monolayer Grating: CO on Ni(111)," *Optics Lett.* **14**, 503 (1989); LBL-26276.

Other Publications

6. Y.R. Shen, "Optical Second Harmonic Generation at Interfaces," *Ann. Rev. Phys. Chem.* **40**, 327 (1989); LBL-26840.
7. W. Chen, M. Feller, J. Huang, R. Superfine, and Y.R. Shen, "Nonlinear Optical Studies of Molecular Orientation and Alignment at Interfaces," *Bull. Am. Phys. Soc.* **34**, 1678 (1989); LBL-27547abs.
8. X.D. Zhu, Th. Rasing, and Y.R. Shen, "Measurement of Surface Diffusion by Second Harmonic Generation from a Monolayer Grating," in *Conf. Quantum Electronics and Laser Conf. 1989 Technical Digest Series*, Vol. 12, Optical Society of America, Washington, DC, 1989, paper TUDD1; LBL-26491abs.
9. Y.R. Shen and G.Z. Yang, "Theory of Self-Phase Modulation and Spectral Broadening," in *The Supercontinuum Laser Source*, R.R. Alfano, Ed., Springer-Verlag, Berlin, 1989, p. 1; LBL-25040.

LBL Reports

10. X.D. Zhu and Y.R. Shen, "Multipolar Contributions to Optical Second-Harmonic Generation in Isotropic Fluids," *Phys. Rev. A (Comment)* (in press); LBL-26841.
11. X.D. Zhu (Ph.D. Thesis), "Nonlinear Optical Studies of Adsorbates: Spectroscopy and Dynamics," LBL-27694.
12. Y.R. Shen, "Nonlinear Interaction of Surface Polaritons," submitted to *Phys. Reports*; LBL-27722.

Invited Talks

13. Y.R. Shen, "Nonlinear Optics and Surface Science," Michigan State University, E. Lansing, Jan. 9, 1989.

14. Y.R. Shen, "Nonlinear Optics for Surface Studies," Ontario Laser and Lightwave Research Center Seminar, Toronto, Jan. 10, 1989.
15. Y.R. Shen, "Optical Studies of Molecules at Interfaces," Gordon Research Conference on Electrochemistry, Ventura, CA, Jan. 16-20, 1989.
16. Y.R. Shen, "Nonlinear Optical Surface Probes," Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlanta, GA, Mar. 6-10, 1989.
17. Y.R. Shen, "Surface Studies by Nonlinear Optical Techniques," Digital Equipment Corp., Palo Alto, CA, Mar. 27, 1989.
18. M.W. Kim, Th. Rasing, and Y.R. Shen, "Two-Dimensional Phase Transitions of a Surfactant Monolayer," Conference on Phase Transitions in Soft Condensed Matter, Geilo, Norway, Apr. 4-14, 1989.
19. Y.R. Shen, "Optical Second Harmonic and Sum-Frequency Generation for Surface Studies," American Chemical Society Meeting (Debye Award Symposium), Dallas, TX, Apr. 10-15, 1989.
20. Y.R. Shen, "Nonlinear Optical Probing of Surfaces," IBM Almaden Research Center, San Jose, CA, Apr. 21, 1989.
22. Y.R. Shen, "Introduction to Nonlinear Optics," Symposium on Laser Applications to Surface Science, Tsinghua University, Taiwan, Republic of China, May 22, 1989.
23. Y.R. Shen, "Surface Studies by Nonlinear Optics," Symposium on Laser Applications to Surface Science, Tsinghua University, Taiwan, Republic of China, May 23, 1989.
24. Y.R. Shen, "Laser-Cooled Trapped Ions," National Taiwan University, Taiwan, Republic of China, May 26, 1989.
25. Y.R. Shen, "Introduction to Nonlinear Optics," Department of Physics, Seoul National University, Republic of Korea, May 29, 1989; Korea Advanced Energy Research Institute, Seoul, Republic of Korea, May 31, 1989.
26. Y.R. Shen, "Surface Studies by Nonlinear Optics," Department of Physics, Korea University, Seoul, Republic of Korea, May 30, 1989.
27. Y.R. Shen, "Applications of Nonlinear Optics to Interfacial Studies," Symposium on Interfacial Phenomena: Structure and Thermodynamic Properties, Victoria, BC, June 4-8, 1989.
28. R. Superfine, J. Huang, and Y.R. Shen, "Conformation, Orientation, and Interaction in Molecular Monolayers: A Surface Second Harmonic and Sum Frequency Generation Study," 9th International Conference on Laser Spectroscopy, Bretton Woods, NH, June 18-23, 1989.
29. W. Chen, M. Feller, J. Huang, R. Superfine, and Y.R. Shen, "Nonlinear Optical Studies of Molecular Orientation and Alignment at Interfaces," 5th Interdisciplinary Laser Science Conference, Stanford, CA, Aug. 27-31, 1989.
30. Y.R. Shen, "Second Harmonic Generation from Metal Solution Interfaces," DOE Basic Energy Science Corrosion Contractor's Review, LBL, Sept. 21, 1989.
31. Y.R. Shen, "SHG Studies of the Surface Diffusion of Molecules," Chemical Physics Seminar, University of California at Los Angeles, Oct. 2, 1989.
32. Y.R. Shen, "Surface Orientation of Molecules: A Nonlinear Optical Study," 4th International Conference on Unconventional Photoactive Solids, San Jose, CA, Oct. 15-18, 1989.
33. M.W. Kim, D. Peiffer, H. Hsiung, Th. Rasing, W. Chen, and Y.R. Shen, "Study of Polymer Adsorption Phenomena on a Solid Substrate," Fall Meeting, Materials Research Society, Boston, MA, Nov. 27-Dec. 1, 1989.
34. Y.R. Shen, "Recent Progress of Nonlinear Optical Studies of Surfaces," Oak Ridge National Laboratory, Oak Ridge, TN, Dec. 18-19, 1989.

Nonlinear Excitations in Solid-State Systems*

Carson D. Jeffries, Investigator

INTRODUCTION

The central objectives of this program are to experimentally study nonlinear phenomena in solid-state systems and to develop models to explain and predict the observed behavior. Previous work focused on spin waves and plasma waves. The present emphasis is on the novel nonlinear electrodynamics exhibited by high-temperature superconductors of the copper oxide type. The origin of the nonlinearities lies in the microstructures of these ceramic materials, as well as in the existence of a critical state. Observed generic behavior includes very high-order odd harmonic generation in zero dc field; even harmonics in nonzero field; and, at high harmonics and high pump power, very sharp power dips periodic in the dc field. Models are developed that semiquantitatively explain the observed behavior, as well as the complex ac susceptibility, and help characterize the material. This work has a bearing on the problems of flux penetration, pinning, flow, and creep in the intergranular and intragranular regions in $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO).

1. Harmonic Generation in Granular High-Temperature Superconductors (Publications 1 and 3)

Q.H. Lam, C.D. Jeffries, and Y. Kim

The nonlinear electrodynamics arising from the granular structure is studied in YBCO samples subject to uniform and parallel ac and dc magnetic fields in the frequency range $10^2 < f < 10^5$ Hz. A number of novel nonlinear phenomena were discovered: (1) For $H_{dc} = 0$, extensive harmonic generation is observed for all odd harmonics, up to at least $n = 41$. (2) If a small "symmetry-breaking" dc field is applied, then all even harmonics are also generated; the harmonic power shows a sharp dip as large as 60 dB as $H_{dc} \rightarrow 0$. (3) For $H_{ac} \lesssim 10$ Oe, the harmonic power for both even and odd harmonics shows similar sharp dips as the dc field is scanned; the dips are approximately equally spaced for high harmonics. These three phenomena can be semiquantitatively understood,

including the symmetry breaking, in a zero-order model by modeling the granular material as a suitably averaged collection of flux-quantized loops (i.e., a collection of RF SQUIDS) with a distribution of areas so chosen to yield the observed dc magnetization $M(H) \sim \tanh(H)$ in low fields. This model, however, is not unique, nor does it allow an easy calculation of the ac losses nor hysteresis.

To further develop the nonlinear studies into useful probes of important parameters (e.g., fluxon pinning forces) of high-temperature superconductors, additional models are being developed and used to interpret both the harmonic-generation data and some new data on the linear part (i.e., the $n = 1$ component) of the complex ac susceptibility (see abstract 2).

The model under study is an extension and revision of the critical-state model of Bean, Anderson, and Kim ("BAK"), originally proposed in the 1960s as an *ad hoc* and phenomenological explanation of the magnetic properties of type II low-temperature superconductors. The model supposes that a field $H(t) = H_{dc} + H_1 \sin \omega t$ applied parallel to a superconducting cylinder induces circular shielding currents with a unique value of current density J_c , the critical current density, dependent on the local field, H_{loc} , and the fluxon pinning force density α , arising from defects and impurities in the sample. The current chooses a radial distribution such that the applied field is exactly shielded out. This model naturally explains the observed hysteresis in the dc magnetization $M(H)$ and the ac loss mechanism in the complex ac susceptibility. It can also explain the harmonic generation.

To apply the original BAK model to granular high-temperature superconductors, it is being extended and modified in three ways: (1) The field dependence of the critical current is assumed to be the more general form $J_c(H) \approx \alpha / (|H_{loc}| + H_0)^\beta$. (2) Two separate contributions to the susceptibility are introduced: the intergranular Josephson junction region, and the intragranular region, i.e., within the superconducting grains themselves; α is small in the first region and quite large in the second. (3) The BAK model predicts sample spatial profiles of $J_c(r)$ that are discontinuous; this is unphysical, and a smoothing is introduced.

Extensive data for the harmonic power $P_n(H_{dc})$ for all harmonics up to $n \approx 10$ are found to be in good agreement with the model, assuming $\beta \approx 2$ (see Figure 1-1). The data are not well explained by the original BAK model (with $\beta = 1$), nor with the above-zero-order model. For sintered pellet samples, the data suggest that the intergranular component is dominant. If the pellet is then ground to a powder, the

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Figure 1-1. (a) Experimental data at 77 K on harmonic generation power $P_n(f)$ (10 dB/div) in a cylindrical ceramic rod of YBCO of 2.5 mm diameter and 1.93 cm length, at frequency 10.5 kHz and ac field amplitude $H_1 = 13.5$ Oe. (b) Prediction according to the modified critical-state model in text, using parameters $H_0 = 4.0$ Oe, $\alpha = 1029$, $\beta = 2.0$. (c) Same as (a), except $H_1 = 4.5$ Oe. (d) Same as (b), except $H_1 = 4.5$ Oe. (XBL 902-346)

data are quite different and suggest a significant intragranular contribution.

2. Complex ac Susceptibility of Granular High-Temperature Superconductors (Publication 3)

Y. Kim, C.D. Jeffries, and Q.H. Lam

A complete and systematic study of the real (χ') and imaginary (χ'') parts of the susceptibility is undertaken,

including the dependence on temperature T , ac magnetic field H_1 , frequency f , and dc magnetic field H_{dc} . A detailed comparison of data with that predicted by the modified critical-state model (see abstract 1) shows promising agreement and allows one to find the field dependence of the critical current and the fluxon pinning force density. These parameters are important for practical applications.

The measurements of χ' and χ'' are performed with a computer-controlled complex-impedance analyzer, which allows for precise digital control of H_1 , H_{dc} , and f . There were two major findings: (1) Both χ' and χ'' depend strongly on H_1 and H_{dc} ; χ'' increases monotonically with H_1 and reaches a maximum at a value that can be shown to be the field H^* for penetration to the center of the cylindrical sample; χ' shows a monotonic increase with H_1 , to a saturated value; this behavior is closely predicted by the model. Much of the data can be understood by the expression for $J_c(H)$ in abstract 1 with the parameter $\beta \approx 2$; this is a steeper dependence of critical current than that originally assumed by BAK for low-temperature type II superconductors. (2) Both χ' and χ'' as a function of H_{dc} , scanned from -40 to $+40$ Oe (see Figure 2-1), show experimental behavior that is also well explained by the model. The data generally indicate that for low fields ($H \lesssim 20$ Oe), the intergranular region is dominant; at $H \gtrsim 100$ Oe the intragranular region becomes dominant.

Figure 2-1. (a,c): Measured real (χ') and imaginary (χ'') parts (MKS units) of ac magnetic susceptibility of a cylindrical YBCO sintered pellet of radius $R = 0.85$ mm and length 10.2 mm. The data are given for several values of the ac field H_1 (Oe). (b,d): Calculated complex ac susceptibility from the modified critical-state model (text) using $R = 0.85$ mm, $H_0 = 3.0$ Oe, $H^* = 8.0$ Oe, and $\beta = 2.25$. (XBL 902-545)

3. Work in Progress

Much remains to be done to understand the complex problem of the electrodynamics of granular superconductors. The above studies are being extended to other compounds (e.g., $\text{Bi}_4\text{Sr}_3\text{Cu}_7\text{O}_x$), as well as a variety of forms (films, single crystals, powders), and to fields $H_{dc} > 10^3$ Oe, where intragranular behavior becomes dominant and the hysteresis is very large and strongly temperature dependent. A new phase-coherent harmonic lock-in detector is under construction that will directly record the in-phase and out-of-phase components of the harmonic voltage, V_n' and V_n'' , for $n = 1, 2, \dots, 20$, providing separate information on both the inductive and the loss components, and thus a more sensitive test of models. An extension of ac frequencies from 10^5 to 10^9 Hz is expected to yield information on the pinned vortex lattice.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. Q.H. Lam and C.D. Jeffries, "Harmonic Generation and Flux Quantization in Granular Superconductors," *Phys. Rev. B* **39**, 4772 (1989); LBL-26227.
2. Y. Kim, "Multifractal Structure of Attractors at the Quasiperiodic Transition to Chaos for Electron-Hole Plasma Instability in Ge," *Phys. Rev. A* **39**, 4801 (1989); LBL-26200.
3. C.D. Jeffries, Q.H. Lam, Y. Kim, M.P. Klein, C.M. Kim, and A. Zettl, "Nonlinear Electrodynamics in the Granular Superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$: Experiments and Interpretation," *Phys. Rev. B* **39**, 11526 (1989); LBL-26624.

Time-Resolved Spectroscopies in Solids*

Peter Y. Yu, Investigator

INTRODUCTION

The purpose of this program is to study the properties of both bulk semiconductors and semiconductor quantum wells fabricated from GaAs and related compounds. One focus of this program is ultrafast processes in semiconductors, which can be studied only by subpicosecond laser pulses generated by actively or passively mode-locked dye lasers. The short laser pulses are used to excite dense electron-hole plasmas in the sample. The dynamics of the hot electron and hot optical phonons are studied by time-resolved Raman scattering or photoluminescence. The effect of carrier screening on the cooling of the hot electrons is studied by varying the photoexcited electron density.

The effects of pressure on the electrical and optical properties of solids are also studied using diamond anvil high-pressure cells. The effect of pressure on defect levels in semiconductors has been studied by capacitance transient techniques. Pressure-induced insulator-to-metal transitions have been studied by measuring the temperature dependence of resistivity as a function of pressure.

1. Subpicosecond Cooling of Hot Electrons and Phonon Temperature Overshoot in GaAs and Related Semiconductors (Publications 14-16)

D. Kim and P.Y. Yu

The relaxation of hot electrons and phonons excited by subpicosecond laser pulses has been studied in GaAs and InGaAs by time-resolved Raman scattering as a function of photoexcited carrier density. Transient overshoot of the longitudinal optical phonon temperature above that of the electron temperature has been observed in GaAs. This result has been explained by the rapid cooling of hot electrons in the lowest conduction-band valley via intervalley scattering. From analysis of the data, the intervalley scattering deformation potentials have been determined in GaAs and in InGaAs.

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2. Discovery of a New Photoinduced Level Related to the DX Centers in AlGaAs Alloys Doped with Si (Publication 7)

P.Y. Yu

When intense white light is shined on a Schottky barrier formed on $\text{Al}_{0.38}\text{Ga}_{0.62}\text{As}$ samples doped with Si, the deep-level transient spectra due to the DX centers are found to be significantly altered. A new peak appeared at lower temperatures. Analysis of the capacitance transients at low temperatures and of the deep-level transient spectra suggests that a new level shallower than the DX center has been induced by the radiation. The contribution of this shallower level is comparable to that of the DX center, thus suggesting that this new level may be related to the DX center.

3. Pressure-Induced Semiconductor-to-Metal Transition in GaAs (Publication 5)

D. Erskine[†] and Y. Yu

Using the diamond anvil cell, temperature-dependent resistivity has been measured in GaAs as a function of pressure. GaAs was found to undergo a semiconductor-to-metal transformation at a pressure of 170 kbar. Above this pressure the resistivity of GaAs decreased approximately linearly with temperature, as expected in a metal. Furthermore, the sample exhibited a superconducting transition to a zero-resistance state at a critical temperature of about 4.5 K.

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1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. N.M. Johnson, W. Shan, and P.Y. Yu, "Pressure Dependence of the P_b Center at the (111) Si-SiO₂ Interface," *Phys. Rev. B* **39**, 3431 (1989); LBL-26396.
2. M.F. Li, P.Y. Yu, W. Shan, W. Hansen, and E.R. Weber, "Effect of Boron on the Pressure Induced Deep Donors in GaAs:Si," *Appl. Phys. Lett.* **54**, 1344 (1989); LBL-25329.
3. G. Martinez, M.F. Li, and P.Y. Yu, "Photoionization of the DX Centers in GaAlAs Alloys and of the Pressure Induced Deep Donors in GaAs:Si," *Defect and Diffusion Forum* **62/62**, 97 (1989).

4. M.F. Li, Y.B. Jia, P.Y. Yu, J. Zhou, and J.L. Gao, "Negative U Property of the DX Center in $\text{Al}_x\text{Ga}_{1-x}\text{As:Si}$," *Phys. Rev. B* **40**, 1430 (1989); LBL-27264.
5. S. Zheng, D. Erskine, M.L. Cohen, and P.Y. Yu, "Metallic Properties of Orthorhombic High Pressure Phase of GaAs: Theory and Experiment," *Solid State Commun.* **71**, 369 (1989); LBL-26543.
6. W. Shen, P.Y. Yu, M.F. Li, W.L. Hansen, and E. Bauser, "Pressure Dependence of the DX Center in $\text{Ga}_{1-x}\text{Al}_x\text{As:Te}$," *Phys. Rev. B* **40**, 7831 (1989); LBL-27262.
7. Y.B. Jia, M.F. Li, J. Zhou, J.L. Gao, M.Y. Kong, P.Y. Yu, and K.T. Chan, "Discovery of a New Photoinduced Electron Trap State Shallower than the DX Center in Si Doped $\text{Al}_x\text{Ga}_{1-x}\text{As}$," *J. Appl. Phys.* **66**, 5632 (1989); LBL-28177.
8. N.M. Johnson, W. Shan, and P.Y. Yu, "Pressure Dependence of the P_b Center Measured by Voltage Transient Spectroscopy," *Semicond. Sci. Technol.* **4**, 1036 (1989); LBL-28346.
9. N.M. Johnson, W. Shan, and P.Y. Yu, "A Test of the Dangling-Orbital Versus Overcoordination Models for the P_b Center at the Si- SiO_2 Interface," *Appl. Surf. Sci.* **39**, 301 (1989).
12. W. Shan, M.F. Li, P.Y. Yu, W.L. Hansen, and W. Walukiewicz, "Pressure Dependence of Schottky Barrier Height at Pt/GaAs Interface," in *Defects in Semiconductors*, G. Ferenczi, Ed., Materials Science Forum **38-41**, 1427 (1989); LBL-26691.
13. M.F. Li, P.Y. Yu, W. Shan, W.L. Hansen, and E.R. Weber, "A Comparison of the Pressure-Induced Deep Donors in GaAs:Si and the DX Centers in GaAlAs:Si Alloys," in *Proc. 19th Int. Conf. Physics of Semiconductors*, W. Zawadzki, Ed., Institute of Physics, Polish Academy of Sciences, Warsaw, Poland, 1988, p. 1051; LBL-25689.

LBL Reports

14. D. Kim and P.Y. Yu, "Photon Temperature Overshoot in GaAs Excited by Subpicosecond Laser Pulses," LBL-27263.
15. D. Kim and P.Y. Yu, "Subpicosecond Cooling of Photoexcited Hot Carriers Studied by One-beam Excite-and-probe Raman Scattering," LBL-28178.
16. D. Kim, P.Y. Yu, K.T. Chan, and S.T. Kellert, "Study of Cooling of Hot Carriers and Intervalley Scattering in $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ by Subpicosecond Raman Scattering," LBL-28179.

Other Publications

10. M.F. Li, P.Y. Yu, W. Shan, W.L. Hansen, and E.R. Weber, "Reduction of Capture Barrier Height of Pressure-Induced Deep Donors (DX Center) in GaAs:Si," in *Defects in Semiconductors*, G. Ferenczi, Ed., Materials Science Forum **38-41**, 851 (1989); LBL-25692.
11. M.F. Li, W. Shan, P.Y. Yu, W.L. Hansen, E.R. Weber, and E. Bauser, "Pressure Dependence of the DX Center in $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As:Te}$," in *Defects in Semiconductors*, G. Ferenczi, Ed., Materials Science Forum **38-41**, 1103 (1989); LBL-25690.

Invited Talks

17. P.Y. Yu, "High Pressure Electrical Measurements: Superconductivity and Deep Traps," Condensed Matter Seminar, Applied Physics Department, Stanford University, Stanford, CA, Feb. 9, 1989.
18. P.Y. Yu, "Probing Deep Donors by High Pressure Measurements," General Meeting, American Physical Society, St. Louis, MO, Mar. 2-24, 1989.

Superconductivity, Superconducting Devices, and 1/f Noise*

John Clarke, Investigator

INTRODUCTION

DC Superconducting QUantum Interference Devices (SQUIDS) based on a niobium technology are applied to a wide variety of applications, including geophysics, nuclear magnetic resonance, and the study of noise in high-transition-temperature (T_c) superconductors. Experiments on high- T_c superconductors such as YBaCuO, BiCaSrCuO, or TlCaBaCuO yield information concerning the dependence of the low-frequency magnetic-flux noise on temperature and the microstructure of the materials, and yield the distribution of flux-pinning energies in thermal equilibrium. An excimer laser is used to deposit epitaxial, *in situ* films of YBaCuO in a variety of structures. Multilayers such as YBaCuO-SrTiO₃-YBaCuO enable two superconducting films to cross one another while remaining electrically isolated. This technology is being used in the fabrication of input circuits, such as flux transformers, for high- T_c SQUIDS. Josephson weak links are grown in YBaCuO films with a novel technique in which electrical pulses are applied until the critical current is reduced to the desired value. Sensitive SQUID amplifiers involving a tuned input circuit and a novel Q-spoiler are used to detect nuclear magnetic and nuclear quadrupole resonance in the frequency range of 20–50 MHz. This system is used to study magnetic resonance of surface layers. SQUIDS with superconducting input circuits are able to detect zero-field nuclear magnetic resonance or nuclear quadrupole resonance at frequencies as low as 20 kHz in organic and amorphous materials. These data provide information on the magnetic fields and electric-field gradients at the active nuclei, for example, ¹⁴N in ammonium salts. Submicron tunnel junctions with capacitances of about 10⁻¹⁵ F are cooled to temperatures as low as 20 mK so that the effects of transferring single electrons can be studied. The role of the electrical environment on these junctions is being investigated.

1. Distribution of Flux-Pinning Energies in YBa₂Cu₃O_{7-δ} and Bi₂Sr₂CaCu₂O_{8+δ} (BSCCO) from Flux Noise (Publication 22)

M. J. Ferrari, M. Johnson, F. C. Wellstood, J. Clarke, D. Mitzi,[†] P. A. Rosenthal,[†] C. B. Eom,[†] T. H. Geballe,[†] A. Kapitulnik,[†] and M. R. Beasley[†]

Much attention has been focused on the vortex pinning energy $U(T)$ of high- T_c superconductors because of its significance in determining the critical current of these materials. Previous experiments to measure $U(T)$ include the study of the resistance transition in a high magnetic field, and the investigation of flux creep. In these experiments, the flux vortices overlap strongly, and large forces are exerted on them by the applied fields and currents. In contrast, the present experiment probes $U(T)$ by means of the magnetic-flux noise generated by the vortices in the absence of applied fields or currents.

A Nb-PbIn thin-film dc SQUID is attached to a sapphire plate maintained at 4.2 K inside a vacuum can. The high- T_c sample is supported approximately 100 μm from the SQUID and parallel to it by a thermally isolated stage that regulates the sample temperature from 4.2 K to 140 K. The motion of the vortices in the high- T_c material is detected as a change in flux through the SQUID and produces noise with a 1/f-like spectral density. This noise can be analyzed on the assumption that it arises from the incoherent superposition of many thermally activated hopping processes, each yielding a Lorentzian power spectrum with a characteristic time τ . The power spectrum of all these processes is the convolution of the Lorentzian function with the distribution of pinning energies $D(U_0)$. This integral can be deconvolved to find $D(U_0)$.

The inferred values of $D(U_0)$ are shown in Figure 1-1 for three samples. The two YBa₂Cu₃O_{7-δ} (YBCO) films show a peak in $D(U_0)$ just below 0.1 eV. In addition, YBCO(1) shows an additional peak at about 0.35 eV that may arise from a-axis grains or possibly grain boundaries. In BSCCO, $D(U_0)$ has a rapid onset near 0.03 eV and peaks near 0.2 eV. These are the first determinations of $D(U_0)$ in thermal equilibrium.

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Figure 1-1. Density of zero-temperature activation energies $D(U_0)$ vs U_0 for (a) a sputtered, post-annealed sample of YBCO; (b) a sputtered, *in situ*-grown sample of YBCO; and (c) a single crystal of BSCCO. (XBL 897-5154)

2. Low Magnetic-Flux Noise Observed in Laser-Deposited *in situ* Films of $\text{YBa}_2\text{Cu}_3\text{O}_{7-8}$ (Publication 10)

M. J. Ferrari, M. Johnson, F. C. Wellstood, J. Clarke, A. Inam,[†] L. Nazar,[‡] and T. Venkatesan[‡]

The advent of high- T_c superconductors has led to the development of SQUIDs capable of operating at liquid nitrogen temperature, 77 K. However, devices tested to date have exhibited large levels of $1/f$ noise at low frequencies f , and since many applications are at low frequencies, it is crucial to reduce this noise. One source of this noise is the motion of flux quanta trapped in the body of the SQUID. Using the apparatus described in abstract ¹, we have measured the low-frequency flux noise in a series of five YBCO films, thus enabling us to characterize them without the need to build a SQUID.

These experiments clearly demonstrate a reduction in the level of the $1/f$ noise as the quality of the film is improved. We believe this improvement arises from the

reduction of the number of pinning sites as the grain size is increased and the film becomes highly c -axis oriented. The lowest level of noise has been observed in a film grown by laser deposition on a LaAlO_3 substrate; the critical current density was $5 \times 10^6 \text{ A cm}^{-2}$ at 77 K. The spectral density $S_\Phi(f)$ of the noise is shown in Figure 2-1, where we see that the magnitude grows slowly, by a factor of four, as the temperature is increased from 4.2 K to 77 K. When the film was cooled in a magnetic field B , the spectral density scaled linearly in B , as indicated in the inset of Figure 2-1. This result implies that the noise arises from the motion of uncorrelated vortices.

The low level of observed noise has significant implications for SQUIDs. If we express the noise at 77 K as a noise energy $\epsilon(1\text{Hz}) = S_\Phi(1\text{Hz})/2L$ for a SQUID with inductance $L = 100 \text{ pH}$, we find $\epsilon \approx 1.7 \times 10^{-29} \text{ JHz}^{-1}$. Compared with commercially available Nb-based devices operated at 4.2 K, this value is about a factor of 6 greater than that of dc SQUIDs and a factor of 2 *less* than rf SQUIDs. Thus, intrinsic flux noise is not likely to be a serious problem in high- T_c SQUIDs or in flux transformers coupled to them in the near future, provided the films are of sufficiently high quality. It should also be noted that there is no reason to believe the noise in Figure 2-1 is the lowest achievable, and further reductions are entirely possible.

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Figure 2-1. $S_\Phi(1\text{Hz})$ vs temperature for laser-deposited YBCO film in zero applied field. Inset shows $f S_\Phi(f)$ ($3 \text{ Hz} \leq f \leq 30 \text{ Hz}$) at two temperatures vs perpendicular magnetic field in which the film was cooled. (XBL 895-5125)

3. Multilayer $\text{YBa}_2\text{Cu}_3\text{O}_x$ - SrTiO_3 - $\text{YBa}_2\text{Cu}_3\text{O}_x$ Films for Insulating Crossovers (Publication 23)[†]

J.J. Kingston, F.C. Wellstood, P. Lerch, A.H. Miklich, and J. Clarke

If one is to produce electronic circuits based on high-temperature superconductors, it is crucial to develop multilayer thin-film structures. In particular, one requires an insulated crossover, that is, two thin-film superconductors that overlap or cross without electrical connection. Because of the special requirements of the oxide superconductors to grow epitaxially on their substrate, the choice of insulating layers is severely limited. We have chosen SrTiO_3 as the most suitable candidate.

The first layer of YBCO is laser-deposited through a stainless steel mask onto a polished (100) MgO substrate, maintained at 730°C , in the H-shaped configuration shown in Figure 3-1. The oxygen pressure is 190 mTorr. The target is then changed to SrTiO_3 , and the second layer is deposited in the shape of a rectangle. In this process, the substrate is held at 660°C , and the oxygen pressure is again 190 mTorr. The third layer (YBCO) is deposited as two strips. The x-ray diffraction pattern for the trilayer indicates that the YBCO films are predominantly c-axis oriented.

Figure 3-1. Configuration of YBCO- SrTiO_3 -YBCO crossover. (XBL 899-5206)

We measured the electrical properties of the trilayer using a four-terminal arrangement, making contacts to the films with pressed in pellets. Figure 3-2(a) shows resistance R vs temperature T for a typical single-layer YBCO film deposited on MgO. Zero resistance is at $T_{c0} = 87.8$ K, and the transition width ΔT_c is 2 K (10–90%). Figure 3-2(b) and (c) shows R vs T for the lower and upper films of a crossover. The properties are not significantly degraded, with $T_{c0} = 87.3$ K and 87.7 K and $\Delta T_c = 1$ and 3 K, respectively. The resistance of the SrTiO_3 , measured between the lower and upper YBCO strips, increases as the temperature is lowered [Figure 3-2(d)]. At 77 K, the resistance is about $100 \text{ M}\Omega$, corresponding to a resistivity of about $4 \times 10^9 \Omega\text{cm}$. The trilayer process has proved highly reproducible, and we have now completed over 100 crossovers with no shorts between the YBCO films. The crossover is an indispensable component of input coils for SQUIDS, and work is now directed towards this circuit.

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Figure 3-2. Resistance vs temperature for (a) single-layer YBCO film deposited on MgO, (b) lower YBCO film of trilayer, (c) upper YBCO film of trilayer, and (d) SrTiO_3 insulating layer measured between upper and lower YBCO films. (XBL 899-5205)

4. Charge Fluctuations in Small Capacitance Junctions (Publication 24)

A.N. Cleland, J.M. Schmidt, and J. Clarke

There has been considerable interest recently in the properties of normal metal-insulator-normal metal tunnel junctions of submicron dimensions at ultralow temperatures T . These junctions have self-capacitances C of 10^{-15} F or lower, so that the energy required to develop a charge of one electron (e), $e^2/2C$, is large compared to the thermal energy $k_B T$. As a result, it is possible to observe effects due to the tunneling of individual electrons, for example, the "Coulomb blockade," where the tunnel current is severely reduced at voltages below $e/2C$. The current-voltage characteristics are extremely sensitive to applied electric fields and enable one to detect charges of much less than e . Furthermore, there has been recent evidence for the observation of coherent effects in which the rate of tunneling of electrons I/e due to a current I can be synchronized with externally applied microwaves of frequency f . If this effect can be enhanced, it will be an extremely important standard, since the current and frequency are related via the simple relation $I = nef$, where n is an integer.

A major difficulty in this research has been the effects of parasitic capacitance due to the external leads. We have performed an experiment to investigate this problem by fabricating small junctions with high-resistance, thin-film leads very close to them. The configuration is shown in the inset in Figure 4-1(a); the heavy lines represent the high-resistivity leads. Essentially identical junctions were also fabricated with low-resistance leads.

The current-voltage (I - V) characteristics for the low- and high-resistance cases are shown in Figure 4-1(a) and (b), together with the dynamic resistance dV/dI vs I . We observe that for the low-resistance case, the I - V characteristic shows very little evidence for a Coulomb gap, whereas for the high-resistance case, the gap is pronounced. These results have been interpreted using the model circuit inset in Figure 4-1(b). Here, C is the junction capacitance, R_L and L_L are the lead resistance and inductance, and C_S is a shunting capacitance due to the cables connected to the thin-film leads. At $T = 0$, a noise current is generated by zero-point fluctuations in R_L that induce a fluctuating voltage across C , thereby smearing out the Coulomb gap. A quantitative solution to the differential equation representing the model circuit leads to the open circles shown in Figure 4-1(a) and (b); the predictions are in good agreement with the experimental data. These results are the first to explain the effects of the environment on the characteristics of a small junction.

Figure 4-1. I - V characteristics (solid lines) for two junctions at 20 mK with (a) $C = 4 \pm 1$ fF and $R = 23$ k Ω , and (b) $C = 5 \pm 1$ fF and $R = 28$ k Ω . Dots represent predictions of theory. Inset in each figure is dV/dI vs I ; note different current scales. Also inset in (a) is the configuration of junction and leads (not to scale), and in (b) its simplified representation. (XBL 899-5250)

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. P.L. Richards, J. Clarke, R. Leoni, P. Lerch, and S. Verghese, "Feasibility of the High T_C Superconducting Bolometer," *Appl. Phys. Lett.* **54**, 283 (1989); LBL-26113.
2. N.Q. Fan, M.B. Heaney, J. Clarke, D. Newitt, L.L. Wald, E. Hahn, A. Bielecki, and A. Pines, "Nuclear Magnetic Resonance with dc SQUID Preamplifiers," *IEEE Trans. Magn.* **MAG-25**, 1193 (1989); LBL-26234.
3. F. C. Wellstood, C. Urbina, and J. Clarke, "Hot Electron Effect in the dc SQUID," *IEEE Trans. Magn.* **MAG-25**, 1001 (1989); LBL-26236.
4. F. C. Wellstood, C. Urbina, and J. Clarke, "Hot-electron Limitation to the Sensitivity of the dc Superconducting Quantum Interference Device," *Appl. Phys. Lett.* **54**, 2599 (1989); LBL-26638.

5. M.J. Ferrari, M. Johnson, F.C. Wellstood, J. Clarke, P.A. Rosenthal, R.H. Hammond, and M.R. Beasley, "Flux Noise and Flux Creep in YBCO Thin Films," *IEEE Trans. Magn. MAG-25*, 806 (1989); LBL-26237.
6. P. Rosenthal, R.H. Hammond, M.R. Beasley, R. Leoni, P. Lerch, and J. Clarke, "Low Frequency Resistance Fluctuations in Films of High Temperature Superconductors," *IEEE Trans. Magn. MAG-25*, 973 (1989); LBL-26235.
7. J. Clarke, "High T_c SQUIDS Show Enhanced Potential for Application," *ISTEC J.* **2**, 25 (1989); LBL-26705.
8. M.H. Devoret, J.M. Martinis, and J. Clarke, "Devoret, Martinis and Clarke Reply," *Phys. Rev. Lett.* **63**, 212 (1989); LBL-27447.
9. J. Clarke, "Principles and Applications of SQUIDS," *Proc. IEEE* **77**, 1208 (1989); LBL-26445.
10. M.J. Ferrari, M. Johnson, F.C. Wellstood, J. Clarke, A. Inam, X.D. Wu, L. Nazar, and T. Venkatesan, "Low Magnetic Flux Noise Observed in Laser-Deposited *in situ* Films of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$," *Nature* **341**, 723 (1989); LBL-27612.

Other Publications

11. A.N. Cleland, J.M. Schmidt, and J. Clarke, "Electrical Characteristics of Small Tunnel Junctions," March Meeting, American Physical Society, St. Louis, MO, Mar. 20-24, 1989; LBL-26684abs.
12. M.J. Ferrari, M. Johnson, F.C. Wellstood, J. Clarke, D. Mitzi, P.A. Rosenthal, M.R. Beasley, and A. Kapitulnik, "Magnetic Flux Noise Processes in High-Temperature Oxide Superconductors," March Meeting, American Physical Society, St. Louis, MO, Mar. 20-24, 1989; LBL-26683abs.
13. N.Q. Fan, J. Clarke, A. Pines, and E.L. Hahn, "Fourier Transform Zero Field NMR and NQR with dc SQUIDS," March Meeting, American Physical Society, St. Louis, MO, Mar. 20-24, 1989; LBL-26687abs.
14. F.C. Wellstood and J. Clarke, "Electron-phonon Interaction in Normal Metal Films," March Meeting, American Physical Society, St. Louis, MO, Mar. 20-24, 1989; LBL-26686abs.
15. J. Clarke, "SQUID Concepts and Systems," in *Proc. NATO Advanced Study Institute on Superconductive Electronics*, M. Nisenoff and H. Weinstock, Eds., 1989, p. 87; LBL-26444.
16. J. Clarke, A.N. Cleland, M.H. Devoret, D. Esteve, and J.M. Martinis, "Macroscopic Quantum Effects in a Josephson Tunnel Junction," in *Ninth International Conference on Noise in Physical Systems*, Montreal, May 25-29, 1987, C.M. Van Vliet, Ed., p. 161.
17. J. Pelz and J. Clarke, "Flicker (1/f) Noise in Cu and Dilute Alloy Films Due to High Energy Electron and Ion Irradiation," in *Ninth International Conference on Noise in Physical Systems*, Montreal, May 25-29, 1987, C.M. Van Vliet, Ed., p. 507.
18. M.J. Ferrari, M. Johnson, F.C. Wellstood, J. Clarke, D. Mitzi, P.A. Rosenthal, M. R. Beasley, and A. Kapitulnik,

"Magnetic Flux Noise Processes in High-temperature Oxide Superconductors," *Bull. Am. Phys. Soc.* **34**, 644 (1989); LBL-26683abs.

19. A.N. Cleland, J.M. Schmidt, and J. Clarke, "Electrical Characteristics of Small Tunnel Junctions," *Bull. Am. Phys. Soc.* **34**, 563 (1989); LBL-26684abs.
20. N. Q. Fan, J. Clarke, A. Pines, and E. L. Hahn, "Fourier Transform Zero Field NMR and NQR with dc SQUIDS," *Bull. Am. Phys. Soc.* **34**, 736 (1989); LBL-26687abs.
21. F.C. Wellstood and J. Clarke, "Electron-phonon Interaction in Normal Metal Films," *Bull. Am. Phys. Soc.* **34**, 1019 (1989); LBL-26686abs.

LBL Reports

22. M.J. Ferrari, M. Johnson, F.C. Wellstood, J. Clarke, D. Mitzi, P.A. Rosenthal, C.B. Eom, T.H. Geballe, A. Kapitulnik, and M.R. Beasley, "Distribution of Flux Pinning Energies in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ from Flux Noise," accepted by *Phys. Rev. Lett.*; LBL-27651.
23. J.J. Kingston, F.C. Wellstood, P. Lerch, A.H. Miklich, and J. Clarke, "Multilayer $\text{YBa}_2\text{Cu}_3\text{O}_x$ - SrTiO_3 - $\text{YBa}_2\text{Cu}_3\text{O}_x$ Films for Insulating Crossovers," accepted by *Appl. Phys. Lett.*; LBL-27845.
24. A.N. Cleland, J.M. Schmidt, and J. Clarke, "Charge Fluctuations in Small Capacitance Junctions," accepted by *Phys. Rev. Lett.*; LBL-28262.
25. D. Robbes, A.H. Miklich, J.J. Kingston, P. Lerch, F.C. Wellstood, and J. Clarke, "Josephson Weak Links in Thin Films of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ Induced by Electrical Pulses," accepted by *Appl. Phys. Lett.*; LBL-28549.

Invited Talks

26. J. Clarke, "SQUID Magnetometers," Superconductors and their Applications, SC Global 89 — International Superconductor Applications Convention, San Francisco, CA, Jan. 10, 1989.
27. J. Clarke, "Intrinsic Low Frequency Noise in Films of YBCO and its Impact on SQUIDS," SC Global 89 — International Superconductor Applications Convention, San Francisco, CA, Jan. 12, 1989.
28. M. J. Ferrari, "Flux Noise Mechanisms in YBCO and BSCCO," Seventh DOE/BES/DMS Information meeting on High- T_c Superconductivity, LBL, Jan. 27, 1989.
29. J. Clarke, "Macroscopic Quantum Tunneling: Experimental Situation," Aspen Winter Physics Conference on the Physics of Matter at Low Temperatures — Present and Future, Aspen, CO, Jan. 28, 1989.
30. J. Clarke, "High- T_c Superconductivity — A Perspective," Bohemian Club, San Francisco, CA, Mar. 8, 1989.
31. N.Q. Fan, J. Clarke, E.L. Hahn, and A. Pines, "Time-Domain Magnetic Resonance with a SQUID Detector," ENC, Inc., 30th Experimental Nuclear Magnetic Resonance Spectroscopy Conference, Asilomar Conference Center, Pacific Grove, CA, Apr. 2-6, 1989.

32. J. Clarke, "SQUIDS and Materials," Spring 1989 High- T_c Workshop, LBL, May 11, 1989.
33. J. Clarke, "SQUIDS, High Temperature Superconductivity, and Geophysics," Chevron Oil Field Research Company, La Habra, CA, May 31, 1989.
34. J. Clarke, "SQUIDS and the Impact of High- T_c Superconductivity," IBM Almaden, San Jose, CA, June 8, 1989.
35. J. Clarke, "Flux Noise in High Temperature Superconductors," Los Alamos National Laboratory, Los Alamos, NM, June 14, 1989.
36. J. Clarke, "Flux Noise and Pinning Energies in High Temperature Superconductors," Gordon Conference, Wolfboro, NH, June 27, 1989.
37. M.J. Ferrari, M. Johnson, F.C. Wellstood, J. Clarke, D. Mitzi, P.A. Rosenthal, C.B. Eom, T.H. Geballe, A. Kapitulnik, and M.R. Beasley, "Distribution of Pinning Energies in $YBa_2Cu_3O_{7.8}$ and $Bi_2Sr_2CaCu_2O_{8+\delta}$ from Flux Noise," Materials and Mechanisms of Superconductivity Conference — High-Temperature Superconductors, Stanford, CA, July 23–28, 1989.
38. J. Clarke, "Flux Noise and Pinning Energies in High- T_c Superconductors," Technical University of Denmark, Lyngby, Denmark, Aug. 24, 1989.
39. J. Clarke, "Superconducting QUantum Interference Devices," Superconductivity — Microjoule Applications, Cambridge, England, Sept. 8, 1989.
40. J. Clarke, "SQUIDS and the Impact of High-Temperature Superconductivity," Superconductivity — Microjoule Applications, Cambridge, England, Sept. 8, 1989.
41. J. Clarke, "Flux Noise and Pinning Energies in High- T_c Superconductors," University of Trondheim, Norway, Sept. 29, 1989.
42. J. Clarke, "Macroscopic Quantum Tunneling in Josephson Junctions," University of Trondheim, Norway, Sept. 29, 1989.
43. J. Clarke, "Flux Noise and Pinning Energies in High- T_c Superconductors," Technical University of Delft, Holland, Oct. 2, 1989.
44. M.J. Ferrari, M. Johnson, F.C. Wellstood, J. Clarke, D. Mitzi, C.B. Eom, P.A. Rosenthal, T.H. Geballe, A. Kapitulnik, M.R. Beasley, A. Inam, X.D. Wu, L. Nazar, and T. Venkatesan, "Noise Characteristics of HTSC Thin Films," SPIE Symposium on Processing of Films for High- T_c Superconducting Electronics, Santa Clara, CA, Oct. 8–13, 1989.
45. J. Clarke, "Flux Noise and Pinning Energies in High- T_c Superconductors," Birmingham University, England, Oct. 13, 1989.
46. J. Clarke, "Macroscopic Quantum Tunneling," Bristol University, England, Oct. 16, 1989.
47. J. Clarke, "Flux Noise and Pinning Energies in High- T_c Superconductors," Cavendish Laboratory, University of Cambridge, England, Nov. 8, 1989.
48. J. Clarke, "Noise Spectroscopy of Pinning Energies in High- T_c Superconductors," Strathclyde University, Scotland, Nov. 13, 1989.
49. J. Clarke, "Technology of High- T_c SQUIDS," Interdisciplinary Research Center for Superconductivity, University of Cambridge, England, Nov. 21, 1989.
50. J. Clarke, "Flux Noise and Pinning Energies in High T_c Superconductors," Siemens Research Laboratory, Erlangen, Federal Republic of Germany, Nov. 23, 1989; Sixtieth Birthdav Symposium for Albert Schmid, University of Karlsruhe, Federal Republic of Germany, Nov. 24, 1989.
51. J. Clarke, "Superconductors, SQUIDS and Brains," Clare Hall, Cambridge, England, Nov. 28, 1989.
52. J. Clarke, "Flux Noise and Pinning Energies in High T_c Superconductors," Imperial College, London, Nov. 29, 1989.
53. J. Clarke, "Future Prospects for SQUIDS," Oxford Instruments, Oxford, England, Dec. 11, 1989.
54. J. Clarke, "Progress Towards a Technology for Electronics with Thin Films of High Temperature Superconductivity," Philips Research Laboratories, Eindhoven, The Netherlands, Dec. 12, 1989.
55. J. Clarke, "SQUIDS, Present and Future," plenary lecture, 1989 Annual Solid State Physics Conference of the Institute of Physics, Warwick, England, Dec. 21, 1989.

THEORETICAL RESEARCH

Theoretical Studies of the Electronic Properties of Solid Surfaces*

L.M. Falicov, Investigator

INTRODUCTION

The purpose of this program is to study properties of solid surfaces. In particular, the interest is in determining (a) structural properties of surfaces, namely the organization and arrangement of atomic constituents at equilibrium; (b) constitutional properties of the surface, in particular the segregation properties of alloys at the surface as a function of crystal structure, surface orientation, nominal chemical composition, and temperature; (c) electronic structure of surfaces, in particular electron states and electron densities in the neighborhood of the surface; (d) vibronic properties of surfaces; (e) magnetic properties of surfaces, both in magnetic solids (ferromagnetic and antiferromagnetic) and in nonmagnetic solids that may develop a magnetic surface layer; and (f) chemical properties of solids—in particular their catalytic properties—as they are related to all the basic physical properties listed above.

A variety of theoretical techniques and models have been developed to focus on the various properties (band-structure models, many-body electron physics, numerical relaxation techniques), but the emphasis is on physical aspects and their implication to experiments rather than on techniques *per se*.

Since 1978 a collaboration has been established with Dr. Eugene Haller and his group to study a set of unusual impurities in very pure semiconductors. These impurities had never been seen before and include hydrogen complexes, lithium-based complexes, carbon-nitrogen complexes, and ordinary substitutional impurities in an unusual charge state.

1. Dephasing Effects in a Two-Dimensional Magnetic-Breakdown Linked-Orbit Network: Magnesium (Publication 3)

J.K. Freericks and L.M. Falicov

The galvanomagnetic properties of a magnetic-breakdown linked-orbit network with two-dimensional topology were calculated for the case of a stochastic distribution of defects in the network. The results showed excellent agreement with experiments on magnesium and illustrate the transition between a smoothly varying magnetoresistivity (semiclassical regime) and an oscillatory magnetoresistivity (quantum regime).

2. Exact Solution of a Quantum Electron-Phonon System for a Two-Site Periodic Cluster (Publication 4)

C.R. Proetto and L.M. Falicov

The ground state of a one-dimensional electron-phonon system was studied by means of a small-crystal approach: an exact solution of a two-site cluster with two electrons and periodic boundary conditions. A single electron band was considered in the tight-binding approximation, together with two-electron interactions between electrons in the same site (Hubbard model); the electrons are coupled to longitudinal-acoustic phonons through a bilinear interaction. The problem is isomorphic with that of the homopolar diatomic molecule with a vibronic degree of freedom and coupling between the electronic and vibronic modes. In the adiabatic (large-ionic-mass, small-vibrational-frequency) limit there is an analytical solution that indicates that the transition between the nondistorted (weak-coupling) and the distorted (strong-coupling) phases can be either continuous or discontinuous, depending on whether the value of electron-electron interaction is smaller or larger than a critical value. In the extremely high-frequency limit (ionic mass $M \rightarrow 0$), it is also possible to find an analytical solution (for $M = 0$) that shows that the system remains undistorted for any value of the electron-phonon coupling and the electron-electron interaction. In the intermediate case (finite, nonvanishing M), numerical

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solutions exhibit a continuous transition from the nondistorted to the distorted phase.

3. Surface and Thin-Film Photoemission Spectrum of Nickel Metal: A Many-Body Solution to a Two-Dimensionally Periodic Cluster (Publication 6)

C. Chen and L.M. Falicov

An exact solution of a four-site crystal model with periodic boundary conditions, a {001} thin film with face-centered-cubic crystal structure, was studied for the nickel density of electron states, as would be measured in surface-sensitive valence-band photoemission. The object was to study modifications of the many-body electronic structure in the presence of surfaces. The model consists of (a) five d orbitals per site per spin, with nearest-neighbor hopping; (b) a one-electron occupation energy for each orbital; and (c) Coulomb repulsions between electrons on the same site. A realistic local-density-approximation one-electron structure and intrasite electron-electron interactions most generally allowed by atomic symmetry are used. Crystal-field effects and single-particle electronic structure in the nickel-film structure are discussed. The photoemission spectrum was calculated and compared with bulk results. Physical conclusions for the true nickel surface many-body states were drawn.

4. Work in Progress

A complete study of the galvanomagnetic properties of NbSe_3 , in particular magnetoresistance at very high fields and very low temperatures, is being conducted. The large variety of complicated phenomena have been elucidated by analyzing the experiment performed by Prof. R.V. Coleman and his collaborators at the University of Virginia.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. M.L. Cohen and L.M. Falicov, "Magnon-Exchange Pairing and Superconductivity," *Science* **243**, 547 (1989); LBL-26089.
2. D.C. Chrzan and L.M. Falicov, "Theoretical Phase Stability of Incommensurable Spin Structures on the (001) Surfaces of MnO-Type Antiferromagnetic Semiconductors," *Phys. Rev. B* **39**, 3159 (1989); LBL-25875.
3. J.K. Freericks and L.M. Falicov, "Dephasing Effects in a Two-Dimensional Magnetic-Breakdown Linked-Orbit

Network: Magnesium," *Phys. Rev. B* **39**, 5678 (1989); LBL-26182.

4. C.R. Proetto and L.M. Falicov, "Exact Solution of a Quantum Electron-Phonon System for a Two-Site Periodic Cluster," *Phys. Rev. B* **39**, 7545 (1989); LBL-25656.
5. H. Svensmark and L.M. Falicov, "Ginzburg-Landau Theory of Deformable Superconductors," *Phys. Rev. B* **40**, 201 (1989); LBL-26090.
6. C. Chen and L.M. Falicov, "Surface and Thin-Film Photoemission Spectrum of Nickel Metal: a Many-Body Solution to a Two-Dimensionally Periodic Cluster," *Phys. Rev. B* **40**, 3560 (1989); LBL-26910.
7. D.C. Chrzan and L.M. Falicov, "Exactly Soluble Model for Antiphase Boundaries in Binary Ordering Alloys," *Phys. Rev. B* **40**, 8194 (1989); LBL-26937.
8. L.M. Falicov, "Superconductivity, A Brief Introduction to Its Phenomenology and Theories," *IEEE J. Quantum Electronics* **25**, 2358 (1989); LBL-26756.

Other Publications

9. J. Heyman, L. Falicov, and E.E. Haller, "Fano Resonances in Beryllium Doped Silicon," *Bull. Am. Phys. Soc.* **34**, 834 (1989); LBL-26357.
10. L.M. Falicov, "Superconductivity: Phenomenology," in *Proc. First Topical School on Superconductivity*, N.H. Andersen and K. Mortensen, Eds., Risø Publication M-2756, Risø National Laboratory, Roskilde, Denmark, 1988, p. 7; LBL-25678.
11. L.M. Falicov, "1987: Open Problems in Condensed Matter Physics," in *Proc. Third Symposium on Pan American Collaboration in Experimental Physics, Rio de Janeiro, Brazil, Oct. 19-23, 1987*, R. Rubinstein and A.F.S. Santoro, Eds., World Scientific, Singapore, 1989, p. 61; LBL-25687.

LBL Reports

12. R.V. Coleman, M.P. Everson, H.-A. Lu, A. Johnson, and L.M. Falicov, "Effects of High Magnetic Fields on Charge-Density Waves in NbSe_3 ," submitted to *Phys. Rev. B*; LBL-26911.
13. J.K. Freericks and L.M. Falicov, "Two-State One-Dimensional Spinless Fermi Gas," submitted to *Phys. Rev. B*; LBL-27524.
14. D.C. Chrzan, L.M. Falicov, J.M. MacLaren, X.-G. Zhang, and A. Gonis, "Magnetic Structure of {111} Stacking Faults in Nickel," submitted to *J. Appl. Phys.*; LBL-27781.
15. L.M. Falicov and D.C. Chrzan, "Incommensurable Surface Spin Structures in MnO-Type Antiferromagnets," LBL-27218.
16. L.M. Falicov, D.T. Pierce, S.D. Bader, R. Gronsky, K.B. Hathaway, H.J. Hopster, D.N. Lambeth, S.S.P. Parkin, G. Prinz, M. Salamon, I.K. Schuller, and R.H. Victora, "Surface, Interface, and Thin-Film Magnetism," LBL-27883.

Invited Talks

17. L.M. Falicov, "Survey of Current Theories in High-Temperature Superconductivity," DOE Information Meeting, Berkeley, CA, Jan. 27, 1989.
18. L.M. Falicov, "Theoretical Developments in High-Temperature Superconductivity," LBL Workshop, May 11, 1989.
19. L.M. Falicov, "Incommensurable Magnetic Surface Structures for MnO-Type Antiferromagnetic Insulators," 2nd International Workshop on the Magnetic Properties of Low-Dimensional Systems, San Luis Potosi, Mexico, May 23, 1989.
20. L.M. Falicov, "Highly Correlated Metals: Heavy Fermions," Argonne National Laboratory, Argonne, IL, June 13, 1989.
21. L.M. Falicov, "A Small-Cluster Approach to Highly Correlated Metals," IBM Almaden Research Center, San Jose, CA, Sept. 21, 1989.
22. L.M. Falicov, "The State of Condensed Matter Physics, 1989," Fourth Symposium on Pan-American Collaboration in Experimental Physics, Bariloche, Argentina, Nov. 7, 1989.
23. L.M. Falicov, "Superconductivity 1989: A Critical Review," Catholic University of Santiago, Santiago, Chile, Nov. 14, 1989.
24. L.M. Falicov, "The Impact of Physics in the Understanding of the Contemporary World," Chilean Academy of Sciences and the Institute of Chile, in commemoration of the 25th Anniversary of the Institute of Chile, Santiago, Chile, Nov. 14, 1989.
25. D.C. Chrzan, "Magnetic Structure of [111] Stacking Faults in Nickel," Magnetism and Magnetic Materials Conference, Boston, MA, Nov. 28, 1989.

Theoretical Solid-State Physics*

Marvin L. Cohen, Investigator

INTRODUCTION

A significant part of the effort of our theoretical group is being devoted to the possibility of predicting new materials and new properties of materials. In particular, a superhard material, C_3N_4 , was shown theoretically to be metastable. Experimental activity is under way to attempt to verify the prediction. Another area at the cutting edge of this theoretical work is the prediction of new structural phases for hydrogen and superconductivity in hydrogen at high pressure. Research on the high-temperature superconducting oxides continues, and there are collaborations with other researchers at LBL. Other areas of research include the study of surfaces and interfaces, high-pressure properties of solids, and the investigation of the properties of metallic clusters.

1. High-Temperature Superconductivity (Publications 4, 6, and 19)

M.L. Cohen

A recent suggestion for electron pairing in high-temperature superconducting oxides via magnon exchange was investigated in detail. It was found that the estimates for the superconducting transition temperature and the maximum transition temperature obtainable with this mechanism were in error. In addition to correcting the existing theory of high-temperature superconductivity based on magnon exchange, our calculations indicated the expected role of this interaction in these interesting materials.

Two collaborations with Professor Alex Zettl's group on high-temperature superconducting oxides led to a refinement of important parameters describing these systems. This research first involved a careful measurement and analysis of the isotope effect in $YBa_2Cu_3O_7$ and an examination of the stress dependence of $YBa_2Cu_3O_7$ along the c-axis in the normal and superconducting states. The latter work showed that no change is observed in the a-b-plane resistivity. The

superconducting T_c increases with decreasing interplane separation. Some implications of these findings for normal-state conducting mechanisms and for models of high-temperature superconductivity were explored.

Because of the important role of copper oxides in high-temperature superconducting systems, the temperature-dependent electrical conductivities of Cu_2O at pressures up to 500 kbar and of CuO up to 700 kbar were investigated. No phase transitions were observed in CuO at pressures and temperatures up to 700 kbar and 3000 K, but the thermal activation energy decreased linearly with pressure and extrapolates to 0 at about 1 Mbar. For Cu_2O , the high-pressure phase has a resistive thermal activation energy of a few meV and localization behavior below 7 K.

2. Superhard Materials (Publications 3, 9, and 14)

A.Y. Liu, R.M. Wentzcovitch, and M.L. Cohen

The phase diagram of BN is expected to be similar to that of carbon. The bulk modulus has been estimated experimentally by some researchers to be even higher than that of diamond. However, scaling formulas for the bulk modulus derived by our group indicated that the bulk modulus should be in the neighborhood of 369 GPa. To test this formula further, a theoretical equation of state was derived from first-principles pseudopotential calculations. The results were in good agreement with the scaling arguments. To ascertain whether the theory was giving correct predictions, a collaboration with Professor Raymond Jeanloz' group at LBL was undertaken. The experimental results gave excellent agreement with the predicted theoretical calculations.

The success with BN and other predictions using the total-energy pseudopotential method motivated a search for materials having compressibilities that rival diamond. The scaling equations discussed above led to an empirical model that predicts that compounds based on carbon and nitrogen could have very high bulk moduli. A prototype system was chosen, and a first-principles pseudopotential total-energy calculation was performed on the system. The results of the first-principles calculation are consistent with the empirical model and show that materials like C_3N_4 can have bulk moduli comparable to or greater than diamond. It was suggested that materials of this kind could be synthesized in the laboratory.

*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, and by the National Science Foundation under Grant No. DMR8818404.

3. Surfaces and Interfaces of GaAs and AlAs (Publications 16 and 18)

S.B. Zhang, M.S. Hybertsen, S.G. Louie, D. Tomanek, and M.L. Cohen

The quasiparticle band energies for 1×1 and 2×2 GaAs/AlAs(001) superlattices have been calculated from first principles using a self-energy approach. Both superlattices have indirect band gaps. The pseudodirect gaps at the zone center derived from folding of the Brillouin zone are larger than the direct gaps. The calculated results explain the various experimental data quantitatively. Matrix elements for optical transitions near the zone center show significant anisotropy. The effects of disorder on the observed spectra are discussed.

We investigate the quasiparticle band structure and optical properties of a relaxed GaAs(110) surface using a first-principles Green's-function approach. The local fields and the dynamical correlation are fully incorporated in the evaluation of the electron self-energy operator. The results provide a quantitative interpretation of the photoemission, inverse photoemission, and reflectivity spectra observed for this surface. Implications of our theoretical surface band structure for the current controversy between various experimental results for the position of the empty surface band are discussed.

4. High Pressure Properties of GaAs and AlAs (Publications 2 and 11)

S.B. Zhang and M.L. Cohen

We examine proposals for the high-pressure phase of GaAs II using a first-principles pseudopotential approach. An orthorhombic structure is found to have lower energy than those of previously studied β -Sn and NaCl structures at a volume near the point at which the phase transition occurs. The structure and the calculated lattice parameters are in excellent agreement with recent x-ray experiments.

Contrary to current beliefs that GaAs II is a semiconductor or semimetal, we find that the two high-pressure orthorhombic phases of GaAs (GaAs II and GaAs III) are metallic and superconducting with T_c close to 4.3 K. Results from the experimental measurements and first-principles pseudopotential calculations are found to be consistent.

5. Solid Hydrogen at High Pressures: Metallic and Superconducting Properties (Publications 7 and 12)

T.W. Barbee III, A. Garcia, J.L. Martins, and M.L. Cohen

The electronic structure and enthalpy are calculated as a function of pressure for several phases of molecular and metallic hydrogen. For the molecular solid, we offer an alternative interpretation of the recently observed transition at 1.5 Mbar. For the intermediate pressure range from 3.8 ± 0.5 to 8.6 ± 1 Mbar, the most stable structures have low coordination numbers and are anisotropic. Among them, a metallic filamentary primitive hexagonal phase is particularly stable. For higher pressures, the bcc structure is the most stable.

At ambient pressure and low temperatures, hydrogen crystallizes in an insulating molecular phase. The possibility of a transition to a metallic structure at high pressures has been the subject of research for over 50 years. Moreover, it has been recognized for some time that metallic hydrogen could be a superconductor, but estimates of its transition temperature vary widely. Here we present the first *ab initio* calculation of the electron-phonon coupling constant λ in a distorted hexagonal high-pressure (~ 400 GPa) phase of hydrogen; this first-principles approach has successfully predicted superconductivity in compressed silicon. From the calculated value of λ for this structure and using standard BCS-Eliashberg theory, the superconducting transition temperature T_c is estimated to be 230 ± 85 K. Thus, if metallic hydrogen were to be formed in the laboratory in the structure proposed here or in similar structures, it should be superconducting with the highest T_c yet known.

6. Metallic Clusters (Publications 13 and 17)

S. Saito, S.B. Zhang, S.G. Louie, and M.L. Cohen

We have calculated the quasiparticle energies of sodium and potassium clusters using the jellium-sphere-background model for positive-ion cores and the Hedin GW approximation for the self-energies of valence electrons. In the calculation of the screened Coulomb interaction, a new general method to approximate the excitation spectrum of the interacting many-body systems is introduced. The calculated ionization potentials and quasiparticle energies are significantly improved compared to calculations based on the Hohenberg-Kohn-Sham local-density-functional theory.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. S.B. Zhang and M.L. Cohen, "Determination of AB Structures from Atomic Properties," *Phys. Rev. B* **39**, 1077 (1989); LBL-26752.
2. S.B. Zhang and M.L. Cohen, "Theory of the Structure of High-Pressure GaAs II," *Phys. Rev. B* **39**, 1450 (1989); LBL-26753.
3. E. Knittle, R.M. Wentzcovitch, R. Jeanloz, and M.L. Cohen, "Experimental and Theoretical Equation of State of Cubic Boron Nitride," *Nature* **337**, 349 (1989); LBL-26754.
4. M.L. Cohen and L.M. Falicov, "Magnon-Exchange Pairing and Superconductivity," *Science* **243**, 547 (1989); LBL-26089.
5. A.Y. Liu, R.M. Wentzcovitch, and M.L. Cohen, "Atomic Arrangement and Electronic Structure of BC_2N ," *Phys. Rev. B* **39**, 1760 (1989); LBL-26873.
6. S. Hoen, W.N. Creager, L.C. Bourne, M.F. Crommie, T.W. Barbee III, M.L. Cohen, A. Zettl, L. Bernardez, and J. Kinney, "Oxygen Isotope Effect Study of $\text{YBa}_2\text{Cu}_3\text{O}_7$," *Phys. Rev. B* **39**, 2269 (1989).
7. T.W. Barbee III, A. Garcia, M.L. Cohen, and J.L. Martins, "Theory of High-Pressure Phases of Hydrogen," *Phys. Rev. Lett.* **62**, 1150 (1989); LBL-26874.
8. M.F. Crommie, A.Y. Liu, A. Zettl, M.L. Cohen, P. Parilla, M.F. Hundley, W.N. Creager, S. Hoen, and M.S. Sherwin, "c-axis Stress Dependence of Normal and Superconducting State Properties of $\text{YBa}_2\text{Cu}_3\text{O}_7$," *Phys. Rev. B* **39**, 4231 (1989).
9. M.L. Cohen, "Novel Materials from Theory," *Nature* **338**, 291 (1989); LBL-26365.
10. S.B. Zhang, D. Tomanek, M.L. Cohen, S.G. Louie, and M.S. Hybertsen, "Evaluation of Quasiparticle Energies of Semiconductors without Inversion Symmetry," *Phys. Rev. B* **40**, 3162 (1989); LBL-26936.
11. S.B. Zhang, D. Erskine, M.L. Cohen, and P.Y. Yu, "Metallic Properties of Orthorhombic High Pressure Phase of GaAs: Theory and Experiment," *Solid State Commun.* **71**, 369 (1989); LBL-26543.
12. T.W. Barbee III, A. Garcia, and M.L. Cohen, "First-Principles Prediction of High-Temperature Superconductivity in Metallic Hydrogen," *Nature* **340**, 369 (1989); LBL-27273.
13. S. Saito, S.B. Zhang, S.G. Louie, and M.L. Cohen, "Quasiparticle Energies in Small Metal Clusters," *Phys. Rev. B* **40**, 3643 (1989); LBL-26808.
14. A.Y. Liu and M.L. Cohen, "Prediction of New Low Compressibility Solids," *Science* **245**, 841 (1989); LBL-27229.
15. X.W. Wang, S.G. Louie, and M.L. Cohen, "Hydrogen Interactions in PdH_n ($1 \leq n \leq 4$)," *Phys. Rev. B* **40**, 5822 (1989); LBL-27312.
16. S.B. Zhang, M.S. Hybertsen, M.L. Cohen, S.G. Louie, and D. Tomanek, "Quasiparticle Band Gaps for Ultrathin GaAs/AlAs(001) Superlattices," *Phys. Rev. Lett.* **63**, 1495 (1989); LBL-27613.
17. S. Saito and M.L. Cohen, "Jellium-Model Calculation for Monomer and Dimer Decays of Some Potassium Clusters," *Z. Phys. D* **12**, 205 (1989).
18. X. Zhu, S.B. Zhang, S.G. Louie, and M.L. Cohen, "Quasiparticle Interpretation of Photoemission Spectra and Optical Properties of GaAs(110)," *Phys. Rev. Lett.* **63**, 2112 (1989); LBL-27556.
19. L.C. Bourne, P.Y. Yu, A. Zettl, and M.L. Cohen, "High-Pressure Electrical Conductivity Measurements in the Copper Oxides," *Phys. Rev. B* **40**, 10973 (1989); LBL-27418.

Other Publications

20. A.Y. Liu, R.M. Wentzcovitch, and M.L. Cohen, "Atomic Arrangement and Electronic Structure of BC_2N ," in *Graphite Intercalation Compounds: Science and Applications*, M. Endo, M.S. Dresselhaus, and G. Dresselhaus, Eds., MRS, Pittsburgh, 1988, p. 137; LBL-26873.
21. M.L. Cohen, "Theory of Bands, Bonds, and Optical Properties of Semiconductors," in *Progress on Electron Properties of Solids*, R. Girlanda *et al.*, Eds., Academic, Dordrecht, 1989, p. 3.
22. M.L. Cohen, "Theoretical Perspectives on HTSC," in *Proc. Int. Superconductors Applications Convention*, San Francisco, CA (1989); LBL-26364abs.
23. M.F. Crommie, A.Y. Liu, A. Zettl, and M.L. Cohen, "X-axis Stress Dependence of Normal and Superconducting State Properties of $\text{YBa}_2\text{Cu}_3\text{O}_7$," *Bull. Am. Phys. Soc.* **34**, 515 (1989).
24. L.C. Bourne, P.Y. Yu, A. Zettl, and M.L. Cohen, "Metallization of the Copper Oxides," *Bull. Am. Phys. Soc.* **34**, 515 (1989); LBL-26367abs.
25. R.M. Wentzcovitch and M.L. Cohen, "Theoretical Model for the hep-ber Transition in Mg," *Bull. Am. Phys. Soc.* **34**, 672 (1989).

LBL Reports

26. P.K. Lam, R.M. Wentzcovitch, and M.L. Cohen, "High Density Phases of BN_x ," LBL-26984.
27. M.F. Crommie, A.Y. Liu, A. Zettl, and M.L. Cohen, "Universality of Transport Properties of High- T_c Superconductors," LBL-26985.
28. M.L. Cohen, "Predicting Properties of Solids, Clusters, and Superconductors," in *Electronic Materials: A New Era of Materials Sciences*, J.R. Chelikowsky and A. Franciosi, Eds. (in press); LBL-27592.
29. M.L. Cohen, "Theoretical Overview of Proposed Mechanisms for High Temperature Superconductivity," in *Proc. Ninth Int. Conf. on Vacuum Ultraviolet Radiation Physics* (in press); LBL-27515.
30. M.L. Cohen, D.R. Penn, and T.W. Barbee III, "Limitations on Electronic Mechanisms for High Temperature Superconducting Oxides," LBL-27895.

31. A.Y. Liu and M.L. Cohen, "Structural Properties and Electronic Structures of Low Compressibility Materials: β - Si_3N_4 and Hypothetical β - C_3N_4 ," LBL-27896.
32. M.L. Cohen, "Some Theories of High Temperature Superconductivity," LBL-28154.
33. S. Saito, S.B. Zhang, S.G. Louie, and M.L. Cohen, "Quasiparticle Energies in Small Alkali-Metal Clusters," LBL-28406.
34. B.K. Godwal, C. Meade, R. Jeanloz, A. Garcia, A.Y. Liu, and M.L. Cohen, "Ultrahigh-Pressure Melting of Lead: A Multidisciplinary Study," LBL-28278.

Invited Talks

35. M.L. Cohen, "University Research Laboratories/Projects," U.S.-Japan Dialog, Beckman Center, Irvine, CA, National Academy of Sciences, Jan. 9, 1989.
36. M.L. Cohen, "Theoretical Perspectives on HTSC," International Superconductor Applications Convention, San Francisco, CA, Jan. 12, 1989.
37. M.L. Cohen, "Review of Current Theories of High-Temperature Superconductivity," Seventh DOE/BES/DMS Information Meeting on High- T_c Superconductivity," LBL, Jan. 27, 1989.
38. M.L. Cohen, "High Temperature Superconductivity," College of Letters and Science Executive Board Meeting, International House, University of California, Berkeley, Mar. 9, 1989.
39. M.L. Cohen, "Present Status of Theories for High-Temperature Superconductors," Department of Electrical Engineering and Computer Sciences, University of California at Berkeley, Mar. 13, 1989.
40. M.L. Cohen, "The New High Temperature Superconductors," Department of Physics, Astronomy, and Chemistry Special Lecture, University of Missouri, St. Louis, Mar. 19, 1989.
41. M.L. Cohen, "The New High Temperature Superconductors," School of Science, California State University, Hayward, Apr. 14, 1989.
42. M.L. Cohen, "Perspectives on Theories of High Temperature Superconductivity," Oak Ridge National Laboratory, Oak Ridge, TN, Apr. 27, 1989.
43. M.L. Cohen, "Some Perspectives on High Temperature Superconductivity," Department of Materials Science and Engineering, University of Washington, Seattle, May 8, 1989.
44. M.L. Cohen, "Theoretical Developments in HTS," LBL High- T_c Workshop, May 11, 1989.
45. M.L. Cohen, "Predicting New Solids and Superconductors," Seminar Series: Electronic Materials—The New Era of Materials Science, Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, May 16, 1989.
46. M.L. Cohen, "Some Perspectives on High Temperature Superconductivity," National Institute of Standards and Technology, Gaithersburg, MD, May 19, 1989.
47. M.L. Cohen, "A Simple Model for Metallic Clusters," National Institute of Standards and Technology, Gaithersburg, MD, May 22, 1989.
48. M.L. Cohen, "Prediction of ~ 230 K Superconductivity in Metallic Hydrogen Using First-Principles Theory," Conference on High-Temperature Superconductivity, Institute for Theoretical Physics, University of California, Santa Barbara, June 26, 1989.
49. M.L. Cohen, "Theoretical Overview of Proposed Mechanisms for High Temperature Superconductivity," Plenary Talk, Ninth International Conference on Vacuum Ultraviolet Radiation Physics, University of Hawaii, Honolulu, July 21, 1989.
50. M.L. Cohen, "Predicting Properties of Solids, Clusters, and Superconductors," National Institute of Standards and Technology, Gaithersburg, MD, Aug. 18, 1989.
51. M.L. Cohen, "Some Perspectives on High Temperature Superconductivity," Distinguished Lecturer Series: Texas Center for Superconductivity, University of Houston, Nov. 7, 1989.
52. M.L. Cohen, "Predicting Properties of Solids, Clusters, and Superconductors," Department of Materials Science and Material Engineering, University of California at Berkeley, Nov. 16, 1989.
53. M.L. Cohen, "Some Theories of High Temperature Superconductivity," Materials Research Society Fall Meeting, Boston, MA, Nov. 27, 1989.
54. M.L. Cohen, "Superhard Materials," Meeting of the Scientific and Educational Advisory Committee, LBL, Dec. 1, 1989.

Surfaces, Chemisorption, and Theory of Solids*

Steven G. Louie, Investigator

INTRODUCTION

The goal of this work is to further basic understanding of the electronic and structural properties of solids and materials systems such as surfaces and interfaces. First-principles quantum mechanical calculations are carried out to obtain a microscopic understanding of realistic systems. The research effort encompasses the study of bulk materials, surfaces, chemisorption systems, and interfaces, and the formulation and development of new theoretical techniques for calculating ground-state and excited-state properties. Current projects include work on surface atomic and electronic structures, structural and vibrational properties of solids, electronic excitation spectra of solids, solid-solid structural phase transformations, and metal clusters.

1. Quasiparticle Interpretation of Photoemission Spectra and Optical Properties of GaAs(110) (Publication 6)[†]

X. Zhu, S.B. Zhang, S.G. Louie, and M.L. Cohen

We investigate the quasiparticle band structure and optical properties of a relaxed GaAs(110) surface using a first-principles Green's-function approach. The local fields and the dynamical correlation are fully incorporated in the evaluation of the electron self-energy operator. The results provide a quantitative interpretation of the photoemission, inverse photoemission, and reflectivity spectra observed for this surface. Implications of our theoretical surface band structure for the current controversy between various experimental results for the position of the empty surface band are discussed.

[†]Supported in part (graduate student salary) by NSF Grant No. DMR88-18404.

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2. Variational Quantum Monte Carlo Calculation of Electronic and Structural Properties of Crystals (Publications 9, 12, and 18)[†]

S. Fahy, X.W. Wang, and S.G. Louie

The electronic and structural properties of solids are calculated using a variational quantum Monte Carlo nonlocal pseudopotential approach. Ionization potentials and electron affinities for atoms, and binding energies and structural properties for covalent crystals, are found to be in excellent agreement with experiment. The method has further been applied to compute various single-particle properties for solids, including the single-particle orbital occupancy, electron-pair correlation functions, and quasiparticle excitation energies. The approach employs a correlated many-electron wave function of the Jastrow-Slater form and the exact Coulomb interaction between electrons.

[†]Supported in part (graduate student salary) by NSF Grant No. DMR88-18404.

3. Quasiparticle Energies in Small Metal Clusters (Publication 4)

S. Saito, S.B. Zhang, S.G. Louie, and M.L. Cohen

We have calculated the quasiparticle energies of sodium and potassium clusters using the jellium-sphere-background model for positive-ion cores and the Hedin GW approximation for the self-energies of valence electrons. In the calculation of the screened Coulomb interaction, a new general method to approximate the excitation spectrum of the interacting many-body systems is introduced. The calculated ionization potentials and quasiparticle energies are significantly improved compared to calculations based on the Hohenberg-Kohn-Sham local-density-functional theory.

4. Quasiparticle Band Gaps for Ultrathin GaAs/AlAs(001) Superlattices (Publications 5 and 20)[†]

S.B. Zhang, M.S. Hybertsen, M.L. Cohen, S.G. Louie, and D. Tomaneck

The quasiparticle band energies for 1×1 and 2×2 GaAs/AlAs(001) superlattices have been calculated from first principles using a self-energy approach. Both superlattices have indirect band gaps. The pseudodirect gaps at the zone center derived from folding of the

Brillouin zone are larger than the direct gaps. The calculated results explain the various experimental data quantitatively. Matrix elements for optical transitions near the zone center show significant anisotropy. The effects of disorder on the observed spectra are discussed.

[†]Supported in part (graduate student salary) by NSF Grant No. DMR88-18404.

5. Evaluation of Quasiparticle Energies for Semiconductors without Inversion Symmetry (Publication 3)[†]

S.B. Zhang, D. Tomanek, M.L. Cohen, S.G. Louie, and M.S. Hybertsen

We have generalized the Fourier-space Hybertsen-Louie self-energy approach for quasiparticle energies in semiconductors to cases without inversion symmetry. In the evaluation of the self-energy operator, a complex four-dimensional Fourier space is used to carry out the double Fourier transforms for time and spatial variables independently. The generalized plasmon-pole scheme for including both local fields and dynamical effects is also properly extended to systems without an inversion center. The quasiparticle energies for GaAs and AlAs are calculated with use of this approach, and results in agreement with experimental data are obtained.

[†]Supported in part (graduate student salary) by NSF Grant No. DMR88-18404.

6. Self-Energy Approach to Quasiparticle Energies Using a Density Functional Treatment of Dielectric Screening (Publication 17)

M.S. Hybertsen and S.G. Louie

Many-electron screening effects play a crucial role in determining the quasiparticle excitation energies in solids. The use of density functional treatment of dielectric screening in quasiparticle calculations is quantitatively discussed. In particular, a model dielectric scheme that has shown to be practical and accurate for semiconductors is described.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. X. Zhu, S. Fahy, and S.G. Louie, "Ab Initio Calculation of Pressure Coefficients of Band Gaps of Silicon: Comparison

of the LDA and Quasiparticle Results," *Phys. Rev. B* **39**, 7840 (1989); LBL-26082.[†]

2. J.E. Northrup, M.S. Hybertsen, and S.G. Louie, "Quasiparticle Excitation Spectrum for Nearly Free Electron Metals," *Phys. Rev. B* **39**, 8198 (1989); LBL-26485.[†]
3. S.B. Zhang, D. Tomanek, M.L. Cohen, S.G. Louie, and M.S. Hybertsen, "Evaluation of Quasiparticle Energies for Semiconductors without Inversion Symmetry," *Phys. Rev. B* **40**, 3162 (1989); LBL-26986.[†]
4. S. Saito, S.B. Zhang, S.G. Louie, and M.L. Cohen, "Quasiparticle Energies in Small Metal Clusters," *Phys. Rev. B* **40**, 3643 (1989); LBL-26808.[†]
5. S.B. Zhang, M.S. Hybertsen, M.L. Cohen, S.G. Louie, and D. Tomanek, "Quasiparticle Band Gaps for Ultrathin GaAs/AlAs(001) Superlattices," *Phys. Rev. Lett.* **63**, 1495 (1989); LBL-27613.[†]
6. X.-J. Zhu, S.B. Zhang, S.G. Louie, and M.L. Cohen, "Quasiparticle Interpretation of Photoemission Spectra and Optical Properties of GaAs(110)," *Phys. Rev. Lett.* **63**, 2112 (1989); LBL-27556.[†]
7. R.P. Andres, R.S. Averback, W.L. Brown, L.E. Brus, W.A. Goddard III, A. Kaldor, S.G. Louie, M. Moscovits, P.S. Peercy, S.J. Riley, R.W. Siegel, F. Spaepen, and Y. Wang, "Research Opportunities on Clusters and Cluster-Assembled Materials," *J. Mat. Res.* **4**, 704 (1989).

Other Publications

8. M.S. Hybertsen and S.G. Louie, "First-Principles Theory of Semiconductor Surface State Energies," in *Proc. 19th Int. Conf. Physics of Semiconductors*, W. Zawadzki, Ed., Institute of Physics, Warsaw, Poland, 1988, Vol. I, p. 713; LBL-25628.[†]
9. S. Fahy, X.W. Wang, and S.G. Louie, "Quantum Monte Carlo Calculation of the Properties of Atomic Carbon and Diamond," in *Proc. 19th Int. Conf. Physics of Semiconductors*, W. Zawadzki, Ed., Institute of Physics, Warsaw, Poland, 1988, Vol. II, p. 845; LBL-25544.[†]
10. M.F. Li, M.P. Surh, and S.G. Louie, "Spin-orbit Interaction Effects in Zincblende Semiconductors: Ab Initio Pseudopotential Calculations," in *Proc. 19th Int. Conf. Physics of Semiconductors*, W. Zawadzki, Ed., Institute of Physics, Warsaw, Poland, 1988, Vol. II, p. 857; LBL-25543.[†]
11. S.G. Louie, "First Principles Calculation of Quasiparticle Energies at Surfaces and Interfaces: Semiconductor Surface-State Spectra and Band Offsets," in *Solvay Conf. Surface Science*, F.W. de Wette, Ed., Springer Series in Surface Sciences **14**, Springer-Verlag, Berlin, 1988, p. 399; LBL-24467.[†]
12. S.G. Louie, "Variational Quantum Monte Carlo Calculation of Materials Properties," in *Atomic Scale Calculations in Materials Science*, J. Tersoff *et al.*, Eds., MRS Symp. Proc. **141**, 3 (1989); LBL-26360.[†]
13. S.G. Louie, "Theory of Ground- and Excited-State Properties of Solids, Surfaces, and Interfaces: Beyond Density Functional Formalism," in *Atomistic Simulation of*

Materials, V. Vitek and D.J. Srolovitz, Eds., Plenum, New York, 1989, p. 125; LBL-26185.[†]

14. S.G. Louie, "Ab Initio Calculation of Materials Properties," in *Proc. DOE Workshop on Theory, Modeling and Instrumentation for Materials by Design*, R.E. Allen *et al.*, Eds., Oak Ridge National Laboratory Conference Proceedings CONF-8409210, 1989, p. 128.[†]
15. S.G. Louie, "Quasiparticle Excitations at Semiconductor Surfaces," *Bull. Am. Phys. Soc.* **34**, 814 (1989); LBL-26361abs.[†]
16. S.G. Louie, "Quantum Monte Carlo Simulations and Electron Correlations in Solids," *Bull. Am. Phys. Soc.* **34**, 1435 (1989); LBL-26806abs.[†]

LBL Reports

17. M.H. Hybertsen and S.G. Louie, "Self-Energy Approach to Quasiparticle Energies Using a Density Functional Treatment of Dielectric Screening," LBL-27946.[†]
18. S.G. Louie, "Variational Quantum Monte Carlo Calculation of Electronic and Structural Properties of Crystals," LBL-27806.[†]
19. S.G. Louie, "Theory of Electronic Excitations in Solids," LBL-27945.[†]
20. S.B. Zhang, M.L. Cohen, S.G. Louie, D. Tomanek, and M.S. Hybertsen, "Quasiparticle Band Offset at the (001) Interface and Band Gaps in Ultrathin Superlattices of GaAs-AlAs," LBL-28285.[†]

Invited Talks

21. S.G. Louie, "Variational Quantum Monte Carlo Calculation of Materials," International Workshop on Computational Condensed Matter Physics: Total Energy and Force Methods, Trieste, Italy, Jan. 4, 1989.

22. S.G. Louie, "Recent Progress in Predicting Materials Properties," Solid State Seminar, LURE, University of Paris, Orsay, France, Jan. 9, 1989.
23. S.G. Louie, "Quasiparticle Excitations at Semiconductor Surfaces," American Physical Society March Meeting, St. Louis, MO, Mar. 23, 1989.
24. S.G. Louie, "Electron Excitations in Solids," University of Minnesota Seminar Series: Electronic Materials: A New Era of Materials Science, Minneapolis, MN, May 2, 1989.
25. S.G. Louie, "First-Principles Studies of Materials Properties and Electron Correlations," MCSD Annual Review, LBL, May 18, 1989.
26. S.G. Louie, "Quantum Monte Carlo Simulations and Electron Correlation in Solids," APS Computational Physics Topical Group Meeting, Boston, MA, June 8, 1989.
27. S.G. Louie, "Variational Calculation of Electronic and Structural Properties of Crystals," Conference on Quantum Simulation of Condensed Matter Phenomena, Los Alamos, NM, Aug. 10, 1989.
28. S.G. Louie, "Recent Progress in Predicting Materials Properties," Joint Colloquium of the Institute for Solid State Physics and Department of Physics, University of Tokyo, Tokyo, Japan, Aug. 16, 1989.
29. S.G. Louie, "Electron Correlation in Solids—A Quantum Monte Carlo Study," Institute for Solid State Physics, Tokyo, Japan, Aug. 17, 1989.
30. S.G. Louie, "Recent Progress in Predicting the Properties of Solids and Surfaces," Department of Physics, Osaka University, Osaka, Japan, Aug. 21, 1989.
31. S.G. Louie, "Recent Progress in Predicting Materials Properties," Sandia National Laboratory, Albuquerque, NM, Oct. 20, 1989.

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MATERIALS CHEMISTRY

SYNTHESIS AND CHEMICAL STRUCTURE

Low-Temperature Properties of Materials*

Norman E. Phillips, Investigator

INTRODUCTION

The objective of this program is to obtain information that contributes to an understanding of the behavior of materials by the measurement of their low-temperature properties, particularly specific heats. There are numerous special cases in which specific-heat data provide either a test of theoretical models or values of important parameters that could not otherwise be obtained. Since much of the work is in the region below 1 K, where the temperature scale is not well established, and because accurate temperature determinations are important for specific-heat measurements, research is also conducted on methods of temperature measurement. An accurate temperature scale that extends to 5 mK has been developed. The interest in high- T_c superconductors has led to an extension of the measurement capabilities to above 100 K. Recent specific-heat measurements include measurements on a number of heavy-fermion compounds, including three of the four known heavy-fermion superconductors and Th-doped UBe_{13} ; and measurements on high- T_c superconductors that have given a measure of the fraction of bulk superconductivity and given estimates of the electronic density of states.

Future objectives include additional studies on high- T_c superconductors, and specific-heat measurements at pressures to 20 kbar and in magnetic fields to 9 T on other heavy-fermion compounds.

*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

1. Specific Heat of $YBa_2Cu_3O_7$ (Publications 8 and 11)

N.E. Phillips, R.A. Fisher, J.E. Gordon,[†] S. Kim, A.M. Stacy, M.K. Crawford,[‡] and E.M. McCarron III[‡]

The concentration, n_2 , of Cu^{2+} moments that order (in zero applied field) below 1 K was determined by measurements of the low-temperature specific heat, C , in magnetic fields. The discontinuity in specific heat at T_c , $\Delta C(T_c)$, decreases approximately linearly with increasing n_2 , showing that these moments are located on the $YBa_2Cu_3O_7$ lattice (see Figure 1-1). The "ideal" value of $\Delta C(T_c)$, the value for a fully superconducting sample, is derived by extrapolation to $n_2 = 0$, and the volume fraction of superconductivity, f_s , for any sample is given by the ratio of $\Delta C(T_c)$ to the ideal value. This measure of f_s is important for evaluating parameters derived from measurements on the superconducting phase and is probably related to the "weak link" effect. Application of this criterion to various data has given measures of the strength of the coupling in the superconducting state and the normal-state electron density of states.

The total concentration, n , of Cu^{2+} moments in $YBa_2Cu_3O_7$ is determined by the high-temperature

Figure 1-1. $\Delta C(T_c)/T_c$ vs n_2 , the concentration of Cu^{2+} moments on the $YBa_2Cu_3O_7$ lattice. (XBL 903-786A)

susceptibility, and the concentration in impurity phases, n_1 , which order near 10 K is then determined as $n_1 = n - n_2$. As shown in Figure 1-2, the coefficient of the low-temperature linear term in C , $\gamma(0)$, is made up of two contributions, one proportional to n_2 and one proportional to n_1 , i.e., there is no evidence for an "intrinsic" contribution. This result is of interest in connection with theories that have predicted the existence of an intrinsic linear term.

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2. Specific Heat of URu₂Si₂: Effect of Pressure and Magnetic Field on the Magnetic and Superconducting Transitions (Publication 9)

R.A. Fisher, S. Kim, Y. Wu, N.E. Phillips, M.W. McElfresh,[†] M.S. Torikachvili,[‡] and M.B. Maple[§]

Specific heats were measured in the range $0.3 \leq T \leq 30$ K for $0 \leq H \leq 7$ T and $P = 0$, and for $H = 0$ and $0 \leq P \leq 6.3$ kbar (see Figure 2-1). For $H = 0$ and $P = 0$, the measurements were extended to 0.15 K. Above the superconducting transition, the $H = 0$ and 7 T data can be superimposed. For the magnetic transition near $T_0 = 18$ K, T_0 increased with increasing P , accompanied by a broadening and attenuation of the specific-heat anomaly. The superconducting transition near $T_c = 1.5$ K was broadened, attenuated, and shifted to lower temperatures for both increasing P and H . The superconducting transition is similar to that of UPt₃, and both the temperature dependence of the superconducting-state specific heat

Figure 1-2. The solid triangles represent $\gamma(0)$ vs n . Correlations of this type have led to the conclusion that there is an intrinsic, nonzero value of $\gamma(0)$ in the superconducting states. The open squares and circles represent n_2 - and n_1 -proportional components of $\gamma(0)$, obtained from the same data. This correlation suggests that $\gamma(0) = 0$ in the limit that both n_1 and $n_2 = 0$. (XBL 897-2700A)

Figure 2-1. C/T vs T in $H = 0$ and 7 T showing the superconducting and magnetic transitions. The solid line is a composite of lattice and crystal-field specific heats. (XBL 896-2345)

anomaly and the derived parameters are consistent with an unconventional polar-type pairing.

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1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. R.A. Fisher, N.E. Phillips, C. Marcenat, J. Flouquet, P. Haen, P. Lejay, and J.-M. Mignot, "Specific Heat of (Ce,Lu)Ru₂Si₂ in High Magnetic Fields," *J. de Physique* (Suppl. 12) **49**, 759 (1988); LBL-25764.
2. R.A. Fisher, S. Kim, B.F. Woodfield, N.E. Phillips, L. Taillefer, K. Hasselbach, J. Flouquet, A.L. Giorgi, and J.L. Smith, "Specific Heat of UPt₃: Evidence for Unconventional Superconductivity," *Phys. Rev. Lett.* **62**, 1411 (1989); LBL-25456.
3. J.E. Gordon, M.L. Tan, R.A. Fisher, and N.E. Phillips, "Specific Heat Data of High- T_c Superconductors: Lattice and Electronic Contributions," *Solid State Commun.* **69**, 625 (1989); LBL-25845.
4. R.A. Fisher, S. Kim, Y. Wu, N.E. Phillips, H.M. Ledbetter, and K. Togano, "Specific Heat of the High- T_c Superconductor (Bi_{1.66}Pb_{0.34})Ca₂Sr₂Cu₃O₁₀," *Physica C* **162-164**, 502 (1989); LBL-27402.
5. N.E. Phillips, R.A. Fisher, S. Kim, B.F. Woodfield, L. Taillefer, K. Hasselbach, J. Flouquet, A.L. Giorgi, and J.L. Smith, "Evidence for Unconventional Superconductivity in UPt₃: Splitting of the Specific Heat Anomaly in T_c ," *Physica C* **162-164**, 413 (1989); LBL-27403.

6. S. Kim, R.A. Fisher, N.E. Phillips, and J.E. Gordon, "Specific Heat of High- T_c $\text{YBa}_2(\text{Cu}_{3-x}\text{M}_x)\text{O}_7$ with $\text{M} = \text{Cr}$ or Zn ," *Physica C* **162-164**, 494 (1989); LBL-27404.
7. J.E. Gordon, R.A. Fisher, S. Kim, and N.E. Phillips, "Lattice and Electronic Specific Heat of $\text{YBa}_2\text{Cu}_3\text{O}_7$," *Physica C* **162-164**, 484 (1989); LBL-27405.
8. N.E. Phillips, R.A. Fisher, J.E. Gordon, and S. Kim, "Origin of the 'Linear' Term in the Specific Heat of $\text{YBa}_2\text{Cu}_3\text{O}_7$," *Physica C* **162-164**, 1651 (1989); LBL-27541.
10. J.E. Gordon, R.A. Fisher, S. Kim, and N.E. Phillips, "Thermal and Magnetic Measurements on $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$," International Conference on Superconductivity (ICSC), Bangalore, India, Jan. 10-14, 1990; LBL-28305.
11. N.E. Phillips, R.A. Fisher, J.E. Gordon, S. Kim, A.M. Stacy, M.K. Crawford, and E.M. McCarron III, "Specific Heat of $\text{YBa}_2\text{Cu}_3\text{O}_7$: Origin of the 'Linear' Term, Volume Fraction of Superconductivity," submitted to *Phys. Rev. Lett.*; LBL-28304.

LBL Reports

9. R.A. Fisher, S. Kim, Y. Wu, N.E. Phillips, M.W. McElfresh, M.S. Torikachvili, and M.B. Maple, "Specific Heat of URu_2Si_2 : Effect of Pressure and Magnetic Field on the Magnetic and Superconducting Transitions," International Conference on the Physics of Highly Correlated Electron Systems, Santa Fe, NM, Sept. 11-15, 1989; LBL-27507.

Invited Talks

12. N.E. Phillips, "The Specific Heat of $\text{YBa}_2\text{Cu}_3\text{O}_7$: The Origin of the Linear Term, and the Volume Fraction of Superconductivity," CNRS/CRTBT, Grenoble, France, Oct. 1989; Technische Hochschule Darmstadt, Federal Republic of Germany, Jan. 1990; Université de Geneve, Geneva, Switzerland, Jan. 1990.

Electrochemical Processes*

Charles W. Tobias, Investigator

INTRODUCTION

This program is designed to advance the scientific foundations of electrochemical engineering and to broaden the range of useful applications of electrochemical transformations. Electrolysis processes have inherent advantages over thermochemical methods with respect to material yield and energy efficiency. However, in spite of their long history of economically significant applications, cell processes have not achieved their potential with respect to performance and range of applications in chemical synthesis, nor in energy conversion or storage. A major reason for this condition is the complex nature of transport phenomena in ionic media, as they are coupled to charge-transfer processes at the electrode surface.

- Multicomponent transport of charged species in solution is described by a mathematical model, and the composition at the surface experimentally determined, to clarify the mechanism of anomalous electrodeposition of magnetic alloys.
- In projects jointly directed with Dr. R.H. Muller, novel methods are explored for the reduction of mass-transfer resistance in high-rate applications, including in electroforming of metals, and in electroorganic synthesis. The effects of suspended inert solid particles in flowing electrolytes, on transport rates, and on electrocrystallization are determined and correlated.

Applied research on the "Surface Morphology of Metals in Electrodeposition," and on "Engineering Analysis of Electrolytic Gas Evolution," is supported by the Assistant Secretary of Conservation and Renewable Energy, Office of Energy Storage and Distribution, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. Results are presented in this Report in the Electrochemical Storage section.

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1. A Mathematical Model for Anomalous Codeposition of Nickel-Iron On a Rotating-Disk Electrode (Publication 4)

S. Hessami and C.W. Tobias

Certain combinations of the members of the iron group, zinc, lead, and tin are known to show a complex behavior when codeposited from acid baths in pH range 2 to 4. The discharge of the more noble component is inhibited, causing the appearance of the less noble component at a much higher ratio in the deposit than in the electrolyte.

The complexity of these systems is partly a consequence of hydrolysis of the metal ions in the solution. Hydrogen evolution takes place simultaneously during metal deposition and causes an increase in pH in the cathodic boundary layer, which in turn leads to a nonuniform degree of hydrolysis. It is important to distinguish the hydrolysis product ions (metal-hydroxide ion complexes) from metal hydroxides (solid-phase precipitates). Hydrolysis product ions, such as FeOH^+ and NiOH^+ , have long been studied. They have much larger dissociation constants than their metal hydroxides, e.g.,

$$K_{\text{Fe}(\text{OH})_2}^{\text{sp}} = 4.84 \times 10^{-17} \text{ vs } K_{\text{FeOH}^+}^{\text{eq}} + 5.78 \times 10^{-8} ,$$

allowing them to be thermodynamically stable at several pH units lower than the hydroxides.

A theoretical model has been developed that includes the effect of metal-hydroxide ions in the mechanism of nickel-iron codeposition. The kinetic parameters of the alloy deposition are assumed to be the same as those of the single metals, involving the discharge of both metal and metal-hydroxide ions; however, during codeposition, the metal-hydroxide ions are allowed to discharge at only a fraction of surface sites proportional to their interfacial concentration. The interfacial concentrations of the metal ions, metal-hydroxide ions, and hydrogen ions are calculated by solving the convective diffusion equations coupled with the homogeneous reactions of water and metal-hydroxide ions. Figure 1-1 compares the recent experimental data of Andricacos *et al.*¹ with the model results.

Application of the model to the codeposition of nickel-iron on a rotating-disk electrode system predicts the following salient features of anomalous deposition: (1) the ratio of the less noble metal (iron) is much higher in the alloy than in the electrolyte; (2) the percentage of the less noble metal as a function of the applied potential goes through a maximum; (3) the presence of the less noble metal inhibits the discharge of the more noble metal (nickel); and (4) current efficiency of alloy deposition increases with applied potential. The effects of agitation

Figure 1-1. Current efficiency η (A) and percentage of iron in the alloy (B) as a function of the absolute value of cathodic potential $V-V_{NHE}$, pH, and agitation rate. Experimental data (dashed lines) taken from Andricacos *et al.*,¹ at a bulk pH of 3: 3600 rpm ($\bullet$), 1,600 rpm ($\blacktriangle$). Model prediction shown by solid lines. Curve 1: pH = 4; 1600 rpm; curve 2: pH = 4; 3600 rpm; curve 3: pH = 3; 1600 rpm; curve 4: pH = 3; 3600 rpm. (XBL 902-437)

and pH on the alloy system were simulated; the results are in qualitative agreement with experimental observations.

1. P. Andricacos, C. Arana, J. Tabib, J. Dukovic, and L.T. Romankiw, *J. Electrochem. Soc.* **136**, 1336 (1989).

2. Enhancement of Mass Transfer to a Rotating Cylinder Electrode by Inert Particles Suspended in the Electrolyte (Publication 5)

L.H. Kim,[†] R.H. Muller, and C.W. Tobias

Mass-transfer rates were investigated for a rotating cylindrical electrode in the presence of suspended particles either more or less dense than the electrolyte. In the case of low-density particles, the limiting-current density for the reduction of ferricyanide increases rapidly with volume fraction of solids up to about 10%, then gradually declines to values near those for the particle-free electrolyte. The

transport process is interpreted by a three-zone model in which mass-transfer rate is controlled by different modes of particle behavior in the centrifugal force field.

For high-density particles, limiting currents increase monotonically with increasing particle concentration, and the enhancement caused by suspended particles decreases with increasing rotation speed.

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1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. P.K. Andersen, R.H. Muller, and C.W. Tobias, "The Effect of Suspended Solids on Mass Transfer to a Rotating Disk," *J. Electrochem. Soc.* **136**, 390 (1989); LBL-24415.
2. D.P. Barkey, R.H. Muller, and C.W. Tobias, "Roughness Development in Metal Electrodeposition. I. Experimental Results," *J. Electrochem. Soc.* **136**, 2199 (1989); LBL-26021.
3. D.P. Barkey, R.H. Muller, and C.W. Tobias, "Roughness Development in Metal Electrodeposition: II. Stability Theory," *J. Electrochem. Soc.* **136**, 2207 (1989); LBL-26022.
4. S. Hessami and C.W. Tobias, "A Mathematical Model for Anomalous Codeposition of Nickel-Iron on a Rotating Disk Electrode," *J. Electrochem. Soc.* **136**, 3611 (1989); LBL-26769.

Other Publications

5. S. Hessami and C.W. Tobias, "A Mathematical Model for Anomalous Codeposition of Nickel-Iron on a Rotating Disk Electrode," Fall Meeting of the Electrochemical Society, Hollywood, FL, Oct. 15-20, 1989, Ext. Abstr. of the Electrochem. Soc., Vol. 89-2, Abstr. No. 312; LBL-26769.

LBL Reports

6. L.H. Kim, R.H. Muller, and C.W. Tobias, "Enhancement of Mass Transfer to a Rotating Cylinder Electrode by Inert Particles Suspended in The Electrolyte," LBL-27473.

Invited Talks

7. S. Hessami and C.W. Tobias, "A Mathematical Model for the Anomalous Codeposition of Nickel-Iron, Including the Effect of Buffering," AIChE Annual Meeting, San Francisco, CA, Nov. 5-10, 1989, Paper No. 105i; LBL-28224.
8. R.F. Knarr, M. Velasco, S. Lynn, and C.W. Tobias, "Electrochemical Reduction of 2-Ethyl Anthraquinone," AIChE Annual Meeting, San Francisco, CA, Nov. 5-10, 1989, Paper No. 104d.

HIGH-TEMPERATURE AND SURFACE CHEMISTRY

High-Temperature Thermodynamics*

Leo Brewer, Investigator

INTRODUCTION

The understanding of high-temperature chemistry is not only important for processes carried out at high temperature, such as those of fusion and fission reactors and fossil-fuel power generators, but it is also important for the preparation and fabrication of ceramics, metals, semiconductors, superconductors, and many other materials. The understanding of high-temperature behavior is complicated by the occurrence of unusual species and phases that are often unstable at conventional temperatures. It is difficult to carry out measurements to obtain the data needed for the design of high-temperature systems. Thus, it is most important to develop broad predictive models that provide reliable prediction of high-temperature behavior. The experiments in progress are aimed at the testing or development of such predictive models.

Previous research of this program has led to the development of a variety of successful models of predictive capability for the behavior of gases, refractory containment materials, and of many metallic systems. At the present time the main thrust of the research is aimed at providing quantitative predictive models for the strongly interacting transition-metal alloys exhibiting generalized Lewis acid-base behavior. A variety of experimental methods are being used to characterize the thermodynamics of these systems.

1. Generalized Lewis Acid-Base Reactions of Metals (Publications 1, 3, and 8)

L. Brewer, B. Ebbinghaus, K. Kruschwitz, S. Leonard, and R. Reddy

This general program was initiated during the Manhattan Project days when it was necessary to predict the high-temperature properties of plutonium and other

substances, so that materials could be developed for their high-temperature processing when they became available. A combination of chemical bonding theory with a framework of thermodynamics was used to predict high-temperature behavior and to point the way to new materials that could be developed to carry out the high-temperature processing.

This program has been quite successful in the following areas: (1) characterization of important molecular species in high-temperature vapors; (2) development of improved refractory materials that can withstand rigorous high-temperature environments; and (3) improvement of understanding of the chemical interactions between atoms and molecules in solutions, particularly metallic alloys. Models based on this background, together with spectroscopic information and thermodynamics, have provided for the successful prediction of multicomponent phase diagrams of the metals. This information has been valuable for the development of new materials to meet the design criteria of new applications.

The present emphasis on strongly interacting combinations of metallic acids and bases is aimed at improving the predictive ability for these systems, which have unique properties of importance for many applications. However, work is continuing toward the improvement of understanding of the behavior of all types of materials at high temperatures.

The present research could be described as the study of an acid-base titration where the acid is an electron-deficient element such as Ti, Zr, V, or Nb, while the base is a metal, such as Rh, Ir, Pd, or Pt, that has excess nonbonding electrons. One procedure for studying the titration is to use an electrochemical cell with solid electrolytes such as thorium doped with yttria. By repeating the electrochemical potential measurements for a series of compositions, the partial molal Gibbs energies of the components can be characterized. This method is limited to rather low temperatures, in the 800 to 1200°C range. For high-temperature studies, gaseous equilibria measurements are being carried out. One fruitful method has been the equilibration of a metal nitride and a metal alloy with nitrogen gas at a fixed pressure to provide the partial molal Gibbs energy of the metal in the alloy. Also, water-hydrogen gaseous mixtures have been equilibrated with oxide-alloy mixtures to obtain thermodynamic data. The many oxide phases of Ti, V, and Nb have been used by equilibrating a pair of adjoining oxides such as NbO₂ and

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Nb₁₂O₂₄, with fixed Nb and O thermodynamic activity, with Pd, for example, and analyzing the Nb content in the equilibrated Pd phase. Vapor pressure measurements for the alloys using mass spectrometry have been used. Measurements on the solid phase have been very difficult because of the very low vapor pressures and difficulty of equilibrating the surfaces of the samples with the bulk. On the other hand, liquid samples in the 2000–3000 K range have been difficult to handle because of attack of containers and creep of the liquid to the top of the vapor pressure cell. Alternative methods using optical emission spectrometry and weight-loss Langmuir measurements have also been used. Comparison of results by these different methods has been useful in providing checks on undetected systematic errors.

In some instances, it has been possible to obtain useful information in the 500–1000°C range by characterizing the solid-phase equilibria. Because of slow attainment of equilibria, a gradient furnace is used that exposes samples to a range of temperatures for periods of a month or more to obtain temperature ranges where equilibrium can be reached. Suitable fluxes added to catalyze the attainment of equilibrium have been found useful. This technique is being used to characterize a wide range of materials in addition to the acid-base systems.

Sufficient data are now available for combinations of Ti, V, Nb, and Zr with Rh, Pd, and Pt to characterize the main features of the variation of base strength of 3d to 4d to 5d electron pairs. Data are being obtained for the enthalpies of formation of intermetallics of Al and Ga and other nontransition metals with the transition metals to extend the acid-base bonding models.

The cell and oxide equilibration measurements have been extended to binary systems of Ti, V, and Nb with Ir and Pt. These data are being used for development of a crystal field model. In addition, the examination of generalized Lewis acid-base interactions has been extended to aluminum as a base interacting with transition metals acting as acids by changing their electronic configurations to dⁿ for most of the transition metals but also to dⁿ⁻¹p for left-hand transition metals. The elimination of electrons from the s orbitals of the transition metals allows Al, Ga, Si, and other nontransition metals with s²pⁿ⁻² ground electronic states to use all of their valence electrons in bonding without having to pay promotion energy to promote one of the s electrons. The interaction of aluminum with transition metals is particularly important, as intermetallics with unique high-temperature properties can be produced. Experiments are under way to characterize the binary Ti-Al system between TiAl and TiAl₃. This work will be extended to ternary systems. An extensive paper has been accepted for publication that discusses the relation between the character of bonding in aluminum alloys and the structure and stability of the resulting phases.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. L. Brewer, "A Bonding Model for Strong Generalized Lewis Acid-Base Interactions In Intermetallics," *Pure and Applied Chem.* **60**, 281 (1988); LBL-23614.
2. L. Brewer, "Standard-State Gibbs Energies of the BCC, HCP, and CCP Structures of Metals," *CALPHAD* **13**, 115 (1989); LBL-24701.
3. L. Brewer, "History of the Application of the Generalized Lewis Acid-Base Theory to Metals," *J. Nucl. Mater.* **167**, 3 (1989); LBL-26942.
4. L. Brewer, "A Conference Overview with a Personal Perspective on the Role of Chemistry in High-Temperature Materials Science and Technology," *High Temp. Sci.* **26**, 100 (1989); LBL-27787.
5. L. Brewer, "Cr-Mo Phase Diagram," *Bull. Alloy Phase Diagrams* **10**, 416 (1989); LBL-28623.

Other Publications

6. J. Margrave, J.F. Ahearne, R.S. Berry, L. Brewer, R.E. Connick, F.L. Culler, Jr., G. Friedlander, P.W. Gilles, C. Ice, C.E. Johnson, H. Kouts, R.K. Lester, E.S. Macias, E.A. Mason, D. Olander, and D. Powers, *Chemical Processes and Products in Severe Nuclear Reactor Accidents: Report of the Workshop on Chemical Processes and Products in Severe Nuclear Reactor Accidents*, National Research Council, 1988.
7. L. Brewer, *Bibliography on the High Temperature Chemistry and Physics of Materials*, Vol. 33, Part 2: Gases: a: Spectroscopy of Interest to High-Temperature Chemistry; B: Reactions Between Gases and Condensed Phases, M.G. Hocking and V. Vasantasree, Eds., IUPAC Commission on High Temperatures and Refractory Materials, London, 1989; LBL-28394.

LBL Reports

8. L. Brewer, "The Nature of Bonding in Transition Metal Aluminides," LBL-27185.
9. L. Brewer, "Ionic Metallic Solutions," LBL-28393.

Invited Talks

10. L. Brewer, "A Conference Overview with a Personal Perspective on the Role of Chemistry in High-Temperature Materials Science and Technology," Plenary Lecture, Sixth International Conference on High Temperature Chemistry of Inorganic Materials, National Institute of Standards and Technology, Gaithersburg, MD, Apr. 3–7, 1989.
11. L. Brewer, "Metallic Bonding," Chemical Dynamics Seminar, University of California at Berkeley, Apr. 26, 1989.
12. L. Brewer, Eyring Lectures in Chemistry: "In What Direction Should Students Concentrate Their Efforts?" "The

- Complexities of High Temperature Science," "Prediction of Two Billion Multicomponent Phase Diagrams," and "Recent Applications of the Generalized Lewis Acid-Base Theory," Arizona State University, Tempe, Sept. 11-16, 1989.
13. L. Brewer, "Physical Organic Concepts Applied to Metallurgy," Brewer Symposium on High Temperature and Materials Chemistry, University of California at Berkeley, Oct. 24, 1989.
 14. L. Brewer, "G.N. Lewis' Definition of Physical Chemistry," G.N. Lewis Era Alumni Reunion address, University of California at Berkeley, Nov. 16, 1989.
 15. L. Brewer, "Bonding in Transition Metal Aluminides," MSNW, Inc., San Marcos, CA, Nov. 23, 1989.

Materials Chemistry Problems in Nuclear Technology*

Donald R. Olander, Investigator

INTRODUCTION

This experimental research program has two principal objectives. The first is concerned with the chemical and physical behavior of materials of nuclear reactor systems, both fission and fusion. The experiments are designed to explore the fundamental processes that underlie the performance of these materials in their service environments, which are characterized by combinations of high temperature, intense radiation fields, and reactive gases or liquids. Corrosion of metals for nuclear applications and high-temperature vaporization of nuclear ceramics are investigated in this program.

The second direction of the project is the study of gas-solid chemical reactions such as corrosion or etching by the method of modulated molecular beams coupled with mass spectrometry. The objective of these studies is to understand the kinetics and mechanisms of such reactions in clean, well-characterized systems. Systems studied include halogen reaction with semiconductors and atomic hydrogen etching of refractory materials.

1. Laser-Pulse Vaporization of Uranium Carbide (Publication 1)

F. Tehranian and D.R. Olander

The kinetics of uranium carbide vaporization in the temperature range 3000–5000 K was studied using a Nd-glass laser with peak power densities about 2×10^5 watts/cm². The vapor species U, UC₂, C₁, and C₃ were detected and analyzed by a quadrupole mass spectrometer. From the mass-spectrometer signals, number densities of the various species in the ionizer were obtained as functions of time.

Free-molecule and gas-dynamic flow models were developed to predict the number densities of molecules in the ionizer using the known surface-temperature transient and equilibrium partial pressures estimated from a previously developed model of UC thermochemistry at temperatures in the liquid range. At low laser energies, the

measured maximum number densities agreed fairly well with the calculated values. At high laser peak-power densities, however, the two differed by factors as large as 10^3 for the uranium species U and UC₂ and by as much as 10^4 for the carbon species C and C₃. Neither UC nor C₂ was detected in the vapor. The experimental ratios of species number densities and the carbon-to-uranium ratio of the vapor were in much better accord with the thermochemical model.

2. Reaction of Atomic Hydrogen with Crystalline Silicon (Publication 2)

J. Abrefah and D.R. Olander

The kinetics of the gas-solid reaction of crystalline silicon, Si(111), and atomic hydrogen (thermally generated in a tungsten oven) has been studied by the modulated-molecular-beam mass-spectrometric technique. Volatile silicon tetrahydride, SiH₄, and recombined molecular hydrogen were the only reaction products detected from ambient temperature to 1000 K. At room temperature the majority of the incident H atoms recombined on the Si surface and was re-emitted as H₂; part of it diffused into the Si lattice; and a small fraction (~3%) reacted to produce SiH₄. The etch rate increased with beam intensity but decreased with increasing temperature. The proposed mechanism involves saturation of the surface dangling bonds by H atoms, formation of SiH and SiH₂ surface complexes, and reaction of the latter with a weakly bound mobile overlayer of H atoms. Rate constants characterizing the elementary steps of the mechanism were determined by fitting the model to the data.

3. Y-Ba-Cu-O Superconducting Films Produced by Long-Pulse Laser Vaporization (Publication 3)[†]

M. Balooch, D.R. Olander, and R.E. Russo[‡]

Deposition of superconducting thin films from YBa₂Cu₃O₇ targets using a long-pulse (ms) Nd-glass laser with 50 J/pulse energy has been demonstrated. The deposition rate was approximately 100 nm/pulse, and the film stoichiometry was close to that of the target. Scanning electron microscopy revealed spherical inclusions in the film. Scanning tunneling microscopy in air showed a terrace-ledge structure on the uniform portion of the film. A film produced by four pulses on a SrTiO₃ substrate held at

*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

540°C and post-annealed in O₂ at 850°C for about 2 hr exhibited an onset transition at 85 K and zero resistance at 82 K. This new approach can provide fast deposition rates and broad-area film coverage per laser shot.

[†]This work was supported by the Director's Exploratory Research and Development Funds of the Lawrence Berkeley Laboratory under Contract No. DE-AC03-76SF00098.

[‡]Permanent address: Applied Sciences Division, Lawrence Berkeley Laboratory.

4. Hydrogen Dissolution in the Release from Nonmetals. I. Uranium Dioxide (Publication 4)

D.F. Sherman and D.R. Olander

A technique was developed for measurement of the solubility and release kinetics of hydrogen in refractory nonmetals. Uranium dioxide specimens were saturated with hydrogen in a high-pressure furnace at pressures between 5 and 30 atm and temperatures from 1200 to 1600°C. Release was accomplished in a separate vacuum extraction apparatus in which the specimen was subjected to a linear temperature ramp. Mass-spectrometric detection of the released hydrogen had a sensitivity of ≈ 2 ng/hr. The equilibrium H/U ratios of hydrogen in single-crystal UO₂ were between 1×10^{-6} and 3×10^{-5} with an apparent heat of solution of 235 kJ/mol. Sievert's law was obeyed. The solubilities of hydrogen in stoichiometric polycrystalline UO₂ were about 10 times larger than in the single crystal, and in polycrystalline UO_{2-x}, about 100 times larger. The hydrogen desorption curves showed multiple peaks, which could not be explained by a simple diffusion mechanism. The kinetics were modeled as first- or second-order detrapping processes.

5. The Kinetics of Molybdenum Etching by Atomic and Molecular Chlorine (Publication 5)

M. Balooch, D.R. Olander, W.J. Siekhaus,[†] and D.E. Miller[‡]

The etching of molybdenum with atomic and molecular chlorine was studied with and without simultaneous bombardment by energetic argon ions. Modulated neutral (molecular or atomic) and ion-beam techniques were used. The studies were carried out in the temperature range 300–1550 K and at molecular chlorine beam intensities 5×10^{15} – 3×10^{17} molecules/cm²sec. The atomic beam was generated by an RF plasma discharge. The main reaction product up to about 1000 K was MoCl₂. The reaction probability with molecular chlorine at room temperature was about 1×10^{-3} . The reaction probability with Cl was a

factor of approximately 10 higher than that obtained with molecular chlorine. An order-of-magnitude increase over the MoCl₂ production was observed at room temperature when the reaction was assisted by energetic argon-ion bombardment.

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6. Work in Progress

A reflectron mass spectrometer has been constructed. It will be used to detect polymolecular clusters produced in the vapor blowoff arising from laser-induced vaporization of refractory oxides. The composition of the vapor produced by laser evaporation of the ternary oxide (U,Nd)O₂ will also be measured by quadrupole mass spectrometry. A theoretical study of the defects in UO_{2±x} will be conducted. The kinetics of corrosion of zirconium by steam is being investigated. The kinetics of the surface reaction of H₂O and UO₂ will be investigated using an electrobalance gravimetric technique.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. F. Tehranian and D.R. Olander, "Laser-Pulse Vaporization of Uranium Carbide," *High Temp. Sci.* **25**, 55 (1989); LBL-24795.
2. J. Abrefah and D.R. Olander, "Reaction of Atomic Hydrogen with Crystalline Silicon," *Surf. Sci.* **209**, 291 (1989); LBL-26315.
3. M. Balooch, D.R. Olander, and R. Russo, "Y-Ba-Cu-O Superconducting Films Produced by Long-pulse Laser Vaporization," *Appl. Phys. Lett.* **55**, 197 (1989); LBL-26414.[†]
4. D.F. Sherman and D.R. Olander, "Hydrogen Dissolution in and Release from Nonmetals I. Uranium Dioxide," *J. Nucl. Mater.* **166**, 307 (1989); LBL-27317.

Other Publications

5. M. Balooch, D.R. Olander, W.J. Siekhaus, and D.E. Miller, "The Kinetics of Molybdenum Etching by Atomic and Molecular Chlorine," in *Tungsten and Other Refractory Metals for VLSI Applications V*, C.M. McConica and R.S. Blewer, Eds., Marcel Dekker, 1989, p. 175.

LBL Reports

6. D.R. Olander, "Laser Vaporization of Refractory Solids," LBL-27779.

7. J. Abrefah, D.R. Dooley, and D.R. Olander, "Reduction of UO_{2+x} by Atomic Hydrogen," LBL-27010.
8. D.R. Olander, Y. Kim, and R.A. Olstad, "The Effective Capacity Method for Transient Heat Conduction and Diffusion Problems with Change of Phase," LBL-28090.
9. J. Abrefah and D.R. Olander, "Hydrogen Dissolution in and Release from Nonmetals—II. Crystalline Silicon, LBL-28020.
10. K. Park and D.R. Olander, "A Defect Model for the Oxygen Potential of Urania — UO_{2+x} ," LBL-27776.
11. A. Motta and D.R. Olander, "Theory of Electronic-Irradiation-Induced Amorphization," LBL-28091.
12. Y. Eyal and D.R. Olander, "Impact of Alpha Decay on Incongruent Actinide Isotope Leaching from Monazite," LBL-27915.
13. D.R. Olander, "Laser-Pulse Vaporization of Refractory Materials," 6th International Conference on High Temperatures, National Institute of Standards and Technology, Gaithersburg, MD, April 1989.
14. D.R. Olander, "Preparation of Thin Films of High- T_c Superconductors by Long-Pulse Laser Vaporization," 26th Bay Area High Temperature Science and Technology Symposium, Sandia National Laboratory Livermore, CA, May 1989.
15. D.R. Olander, "High-Temperature Corrosion of Zirconium," DOE/BES Corrosion Contractors Meeting, Berkeley, CA, Sept. 1989.
16. D.R. Olander, "Thermochemistry of Refractory Oxides," Symposium on High Temperature and Materials Chemistry, Berkeley, CA, Oct. 1989.
17. D.R. Olander, "Dissolution Mechanism of Thorium and Uranium Isotopes from Monazite," 1989 Joint International Waste Management Conference, Kyoto, Japan, Oct. 23, 1989.

Invited Talks

13. D.R. Olander, "Laser-Pulse Vaporization of Refractory Materials," 6th International Conference on High

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Electrochemical Phase Boundaries*

Rolf H. Muller, Investigator

INTRODUCTION

Nucleation and growth processes in the electrosolidification of metals and polymers from aqueous media are investigated to advance the understanding of the development of deposit properties from the first atomic layers to macroscopic thicknesses. Parameters of electrochemical kinetics and mass transfer are studied in the early stages of deposition to gain insight into the action of leveling and brightening agents that control deposit properties. The results of measurements are used to develop theoretical models for the prediction of microstructure and surface morphology and how they depend on deposition conditions in new systems, for which empirical information is not available.

New experimental techniques are developed and used for determining microtopography and composition of deposit surfaces, particularly while immersed in the electrolyte during their formation.

Studies of electrochemical surface layers on battery materials are reported in the section "Electrochemical Energy Storage," Rolf H. Muller, Investigator, in this annual report. Research on electrochemical mass transfer, conducted in collaboration with C.W. Tobias, is reported in his section, "Electrochemical Processes."

1. Roughness Development in Metal Electrodeposition (Publications 4 and 5)

D.P. Barkey, R.H. Muller, and C.W. Tobias

Copper electrodeposits of thicknesses of several hundred μm have been produced by deposition from 1M CuSO_4 , 1M H_2SO_4 on a rotating cylinder at rates up to 5 A/cm^2 (corresponding to 110 $\mu\text{m}/\text{min}$). Digitalized surface profiles were Fourier analyzed to determine roughness amplitudes and spatial periods. For a constant charge passed, a large increase in roughness amplitude was observed with increasing fraction of limiting current at constant current density (see Figure 1-1). A large decrease in roughness amplitude was found with increasing current

Figure 1-1. Roughness amplitude of deposits formed at 0.8 A/cm^2 vs fraction of limiting current. Charge passed: 500 C/cm^2 . Electrolyte: 1.0M CuSO_4 , 1.0M H_2SO_4 at 50°C. Four profiles taken at different positions on one deposit. (XBL 877-3260)

density at constant fraction of limiting current (see Figure 1-2). A moderate decrease of roughness spatial period was observed with increasing current density at constant fraction of limiting current.

A stability analysis for electrodeposition on a substrate with a sinusoidal profile has been formulated. Current distribution was found by a first-order perturbation technique, accounting for ohmic, kinetic, capillary, and concentration overpotentials. The model predictions agree qualitatively with experimental results, if an increase in nucleation density at higher current density is also considered.

2. Effect of Suspended Solids on Mass Transfer to Rotating Disks and Rotating Cylinders (Publications 3 and 7)

K.P. Andersen, L.H. Kim, R.H. Muller, and C.W. Tobias

The enhancement of limiting currents to rotating-disk electrodes by suspended inert particles was studied with particles of equal or greater density than the electrolyte, at

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Figure 1-2. Roughness amplitude of deposits formed at 80% of limiting current vs current density. Charge passed: 500 C/cm². Electrolyte: 1.0M CuSO₄, 1.0M H₂SO₄ at 50°C. Four profiles taken at different positions on one deposit. (XBL 877-3262)

diameters of 1–100 μm and concentrations up to 40 vol%. Torque measurements on the disks showed that increasing the limiting current by the use of suspensions requires significantly less stirring power than by increasing the rotation rate without particles.

With a rotating cylinder, the effect of particles of density lower than that of the electrolyte was found to increase with increasing rotation rate (see Figure 2-1), while it decreased with particles of higher density. The results are consistent with the migration of particles in a centrifugal force field.

3. Ellipsometry as an *In Situ* Probe for the Study of Electrode Processes (Publication 6)

R.H. Muller

The principles of ellipsometry, recent developments in instrumentation, data interpretation, and electrochemical applications have been reviewed. Ellipsometry involves the reflection of polarized monochromatic light from a surface under study and the measurement of two parameters that

Figure 2-1. Variation of limiting-current density $I_{L,*}$ with volume fraction of suspended particles Φ and rotation speed (RPM). Hollow glass beads have diameter of 63–74 μm , density of 0.305 g/cm³; 0.04M K₃Fe(CN)₆, 0.2M K₄Fe(CN)₆, 2M NaOH. (XBL 896-2423)

characterize the change in the state of polarization caused by the reflection.

Ellipsometer measurements are often extremely sensitive to the presence of surface layers, to changes in their thickness or coverage at the level of fractional monolayers, and to changes in surface topography at an atomic scale. The range of film thicknesses that can be observed extends to optical thicknesses of several wavelengths of the light used. Surfaces being studied may be immersed in any optically transparent medium, a characteristic that makes the use of the technique particularly attractive for electrochemical studies.

The use of optical models has made it possible to derive many wavelength-independent surface parameters such as multilayer thicknesses, porosities, or coverages from spectroscopic-ellipsometer measurements. Applications primarily concern the anodic oxidation of metals and semiconductors and the reduction of oxides, corrosion processes and corrosion inhibition, metal deposition, adsorption, and mass transfer.

Future developments are expected to lead to imaging and high-speed spectroscopic instrumentation, the use of off-specular scattered light, and variable lateral coherence. Improvements in the optical theory for composite media and rough surfaces will make it possible to derive better physical data for such systems from the measurements.

4. Work in Progress

The electrodeposition of metals in the presence of inhibitors is being investigated for the deposition of copper with benzotriazole in order to identify the mechanism by

which brightening of the deposit occurs. A bright surface is associated with local roughness much below the wavelength of light. For given mass-transport conditions, brightening has been observed above a critical current density. Scanning tunneling microscopy during deposition has shown an increase in nucleation density by the inhibitor of several orders of magnitude. The resulting small diameter of the growth centers and consequent small-scale roughness generate a bright surface. Work on the role of a possible precipitate layer, the importance of the increase in overpotential caused by the inhibitor, and the incorporation of inhibitor in the deposit is continuing.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. M.J. Armstrong and R.H. Muller, "Island Films Resulting from Ion Bombardment: Spectroscopic Ellipsometry and Auger Electron Spectroscopy," J. Appl. Phys. **65**, 3056 (1989); LBL-25447Rev.
2. M.J. Armstrong and R.H. Muller, "STM Observations of Electrodeposited Copper under Potential Control and Open Circuit," J. Electrochem. Soc. **136**, 584 (1989); LBL-26049.
3. P.K. Andersen, R.H. Muller, and C.W. Tobias, "The Effect of Suspended Solids on Mass Transfer to a Rotating Disk," J. Electrochem. Soc. **136**, 390 (1989); LBL-24415.
4. D.P. Barkey, R.H. Muller, and C.W. Tobias, "Roughness Development in Metal Electrodeposition. I. Experimental Results," J. Electrochem. Soc. **136**, 2199 (1989); LBL-26021.
5. D.P. Barkey, R.H. Muller, and C.W. Tobias, "Roughness Development in Metal Electrodeposition. II. Stability Theory," J. Electrochem. Soc. **136**, 2207 (1989); LBL-26022.

LBL Reports

6. R.H. Muller, "Ellipsometry as an *In Situ* Probe for the Study of Electrode Processes," LBL-23916.
7. L.H. Kim, R.H. Muller, and C. W. Tobias, "Enhancement of Mass Transfer to a Rotating Cylinder by Inert Particles Suspended in the Electrolyte," LBL-27473.

Nuclear Magnetic Resonance*

Alexander Pines, Investigator

INTRODUCTION

The goals of this program are the development of novel theory and experiments in magnetic resonance and the demonstration of their application to materials research. Recent techniques developed in our laboratory include multiple-quantum spectroscopy, zero-field nuclear magnetic resonance (NMR), iterative maps, double rotation (DOR), dynamic-angle spinning (DAS), optical pumping, and SQUID magnetic resonance. Materials applications include clusters, semiconductors, oxides, liquid crystals, zeolites, and intercalated graphite.

1. Oxygen-17 NMR in Solids

B. Chmelka, K.T. Mueller, A. Samoson,[†] J. Stebbins,[‡]
B. Sun, Y. Wu, and J.W. Zwanziger

It is widely lamented that, despite its success with spin-1/2 nuclei such as carbon-13, silicon-29, and phosphorus-31, the popular NMR technique of magic-angle spinning (MAS) is restricted when it comes to important quadrupolar nuclei such as oxygen-17, sodium-23, and aluminum-27, due to second-order broadening. Two new techniques, double rotation (DOR) and dynamic-angle spinning (DAS), involving the rotation of a sample around two axes, overcome these problems. Oxygen-17 DOR and DAS experiments at moderate field have resolved multiple sites in mineral silicates experiments, including clinostatite, forsterite, diopside, larnite, and wollastonite (see Figure 1-1). The DAS experiments have been extended to 2D NMR spectroscopy, allowing the correlation of high-resolution resonances with conventional spinning powder patterns. Current work is under way studying minerals, zeolites, and high-temperature superconductors with these techniques.

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Figure 1-1. Two-dimensional dynamic-angle-spinning spectrum of oxygen-17 in the mineral diopside. The resonances from the three crystallographically distinct oxygen sites are observed in the first frequency dimension and are correlated with anisotropic patterns in the other. The second dimension contains information related to local microstructures at each oxygen site. (XBL 903-1139)

2. High-Resolution Aluminum-27 NMR of VPI-5

Y. Wu, B.F. Chmelka, and M. Davis[†]

Aluminum plays important roles in determining the physical and chemical properties of many interesting materials, for example, the catalytic properties of zeolites. Although NMR spectroscopy is often a sensitive probe of solids, the use of ²⁷Al NMR to investigate the structure of aluminosilicates and aluminophosphates has been severely limited. Anisotropic second-order quadrupolar interactions, responsible for spectral broadening, cannot be eliminated by conventional MAS or multiple-pulse techniques. The first high-resolution NMR spectrum of ²⁷Al in a solid using DOR has been accomplished, and its utility for probing subtle structural perturbations in the aluminophosphate molecular sieve VPI-5 has been demonstrated (see Figures 2-1 and 2-2). These results demonstrate the power of high-resolution ²⁷Al NMR in characterizing molecular structure and adsorbate/host interactions in aluminum-containing materials.

[†]Permanent address: Department of Chemical Engineering, Virginia Polytechnic Institute, Blacksburg, VA 24061.

Figure 2-1. Framework structure of the aluminophosphate molecular sieve VPI-5, showing the hexagonal unit cell with labeled atoms. (XBL 901-133b)

Figure 2-2. ^{27}Al NMR spectra of VPI-5 after dehydration and following two periods of rehydration. Spectra are plotted on arbitrary scales. (XBL 903-979)

3. Berry's Phase in Magnetic Resonance

J. Anandan,[†] M. Koenig, K.T. Mueller, and J.W. Zwanziger

A nondegenerate quantum system undergoing cyclic evolution acquires a geometric (Berry's) phase that is related to the geometry and topology of quantum-state space and the geometry of the system trajectory through this space. These effects are related to the Pancharatnam phase accumulated in a cycle of quantum measurements. Both sorts of phases can be generalized to degenerate systems. Current efforts have resulted in the first direct measurement of non-Abelian geometric effects in a degenerate spin system, and elucidation of the connection between non-Abelian geometric phase and incomplete quantum measurement through generalization of the Pancharatnam phase (see Figure 3-1).

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Figure 3-1. Some possible circuits for geometric phases: cone (circle) (a), spherical triangle (b), slice (or wedge) (c), figure-8 (d), flower (e), and slinky (f). Circuits (a) through (c) have been used to study Abelian geometric phases. The figure-8 (d) would be particularly useful for studying non-Abelian geometric phases, since it encloses no net (oriented) area. Circuits (e) and (f) can be implemented by a double rotor; circuit (f) has been used to study the effects of non-Abelian geometric phase. (XBL 904-1214)

4. Clusters in Solids

B. Chmelka, J. Pearson, and D. Raftery

Two techniques are being further developed to "count" clusters for the purpose of characterizing the distribution of atoms and molecules in solids. The first technique is multiple-quantum NMR, which involves the selective detection of spectroscopic events in which groups of n spins flip and groups of n radiofrequency quanta are absorbed or emitted. The second technique is xenon-NMR, in which the spherical xenon atom is used as a sensitive probe of its surroundings. Problems being studied by these techniques include the distribution of molecules and metal particles in zeolite cavities, clusters of xenon, and the dynamics of dilute spin systems (see Figure 4-1).

Figure 4-1. Room-temperature ^{129}Xe NMR spectra of xenon occluded in NaA zeolite at different loading pressures: 27 atm, 47 atm, 75 atm, and 198 atm. Each peak corresponds to a ^{129}Xe signal from xenon in α -cages containing different numbers of occluded Xe atoms (indicated by the numbers above the respective peaks). The chemical shift is referenced to xenon gas at very low pressure. (XBL 898-7237)

5. Molecules Intercalated in Graphite

D. Caplan, C. Schmidt, and M.F. Quinton[†]

The orientation and motion of tetrahydrofuran (THF) in the ternary graphite intercalation compounds $\text{Cs}(\text{THF})_{1.6}\text{C}_{24}$ and $\text{K}(\text{THF})_{2.5}\text{C}_{24}$ have been determined by means of the proton NMR spectra of highly oriented samples. Line-shape simulations indicate that the THF molecules in $\text{Cs}(\text{THF})_{1.6}\text{C}_{24}$ are oriented with their mean planes parallel to the layers of the host lattice (see Figure 5-1). In $\text{K}(\text{THF})_{2.5}\text{C}_{24}$ the THF molecules appear to be oriented with their mean planes at an angle of about 56° relative to the graphite layers. As a function of the sample orientation with respect to the external magnetic field, the spectra show evidence of (i) a rotation of the THF molecules about the layer normal and (ii) a degree of orientational disorder, corresponding to a mosaic spread of the samples, which was determined by x-ray diffraction.

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6. Multiple-Pulse NMR and Iterative Maps

H. Cho, K.T. Mueller, M. Rosen, S.P. Rucker, A.J. Shaka, and D.N. Shykind

Multiple-pulse schemes used in the extended excitation of spin systems are traditionally derived by average Hamiltonian theory and periodic application of a basic cycle. An alternative approach, stable over a wide range of instrument parameters, involves the application of iterative maps on $\text{SO}(3)$. Fixed points of $U_{n+1} = F(U_n)$ are sought, where U are propagators that are then implemented by

Figure 5-1. Orientations of the THF molecules with respect to the graphite layers in the text. Top: $\text{Cs}(\text{THF})_{1.6}\text{C}_{24}$; bottom: $\text{K}(\text{THF})_{2.5}\text{C}_{24}$. [XBL 904-1215 (top); XBL 904-1216 (bottom)]

means of sophisticated pulse programmers and digital phase shifters. Recent applications include Carr-Purcell trains, spin-decoupling, bistable maps, and coherence transfer in two-dimensional spectroscopy (see Figure 6-1).

Figure 6-1. Two-dimensional basin images through a slice of $SO(3)$, the space of rotations, containing the z -axis. The gray scale at left indicates the number of iterations necessary to map a point. The top map is specified by a premapping step, followed by a phase shift concatenation scheme for NMR pulse sequences. The boundaries of the basin show chaotic flow and nonideal behavior results. The bottom map incorporates inverse pulses and shows smooth flow to the two fixed points of the set: the equator and the z -axis. The dark bands represent an unstable fixed set between the two attractors. Both schemes lead to bandpass behavior as a function of resonance frequency offset in an NMR experiment. [XBB 888-7859 (top); XBB 888-7861 (bottom)]

7. Zero-Field NMR

T. Jarvie, S. Matsui, Z. Olejniczak, B. Sun, and K. Takegoshi

In zero-field NMR, the magnetic field experienced by the sample is cycled between a high value (used for polarization and detection) and zero field, in which spin evolution occurs. This can produce sharp NMR spectra even for polycrystalline or disordered materials and has previously been used to study local symmetry in liquid crystals and correlated motions in hydrogen bonds of solid carboxylic acid dimers. Recent developments involve the application of pulses in zero field, the suppression of zero-frequency peaks, and two-dimensional correlations between high and zero field (see Figure 7-1).

Figure 7-1. Correlation of zero-field and high-field NMR for a powder of proton pairs with various asymmetry of (η) of dipole-coupling. (XBL 888-8948)

8. Magnetic Resonance with a Continuous-Wave SQUID Spectrometer

B. Black, J. Chang, C. Connor, J. Harwood, G. Majer, and A. Pines

In a collaborative project with J. Clarke and E.L. Hahn of CAM and the U.C. Berkeley Physics Department, two new spectrometers have been designed for the direct detection of low-frequency magnetic resonance using dc-SQUID (Superconducting QUantum Interference Device) detectors. Such devices enhance the detection sensitivity by many orders of magnitude. One spectrometer works in continuous-wave (CW) mode by detecting the dc flux induced by a swept radiofrequency source, whereas the second spectrometer detects the time-domain signal following a radiofrequency pulse. Signals with the CW spectrometer have been detected in polycrystalline samples from nuclei such as hydrogen, boron-11, and aluminum-27. Detailed microstructural information can now be obtained in a variety of technologically important materials, such as glasses, zeolite catalysts, polypeptides, and proteins. From a fundamental physics standpoint, this technique now allows us to measure methyl ($-\text{CH}_3$) tunneling rates at low temperatures and to develop techniques for enhancement of signal intensity (see Figure 8-1).

Figure 8-1. Proton NMR spectrum from a single 400-sec sweep of propionic acid at 4.2 K, in a field of 9.3 mT. A sample volume of 0.20 cm^3 was used. The transition between states of the same symmetry, at $\omega_0 = 395 \text{ kHz}$, is flanked by transitions between states of different symmetry, at ω_1 and $\omega_0 + \omega_1$. The tunnel splitting, ω_1 , is measured as 210 kHz. Also visible is the $\Delta m = 2$ transition at $2\omega_0$ near 800 kHz. The inset shows the energy levels for the methyl group. (XBL 896-2467)

9. Optical Pumping

P. Grandinetti, T. Meersman, H. Long, and D. Raftery

New and interesting NMR experiments, such as NMR of surfaces, are often limited by poor signal strength. One promising method to address this signal sensitivity problem is optical pumping, which can dramatically increase the nuclear polarization of rare-gas atoms such as xenon, which is also an interesting NMR probe. Optical pumping of rubidium metal vapor atoms can create an essentially 100% spin-polarized gas that can transfer its polarization to xenon via van der Waals collisions. We have constructed a low-magnetic-field apparatus (see Figure 9-1), and by employing a semiconductor diode laser we can create xenon nuclear polarizations up to 5%, which we detect optically. We have measured longitudinal relaxation times of 30 minutes or longer and are also able to detect a point-by-point free-induction decay, which indicates a reduced relaxation time in the transverse plane due to gas diffusion (see Figure 9-2). The final step is to apply the polarized xenon to samples of interest. We are constructing an apparatus to transport the polarized gas to a high-field NMR probe, where we can use conventional NMR to detect xenon adsorbed on small-surface-area materials.

Figure 9-1. Optical pumping apparatus. (XBL 904-1217)

Figure 9-2. Xenon-129 optically detected free-induction decay (FID). (XBL 904-1218)

10. NMR Studies of Molecular Conformation in Liquid Crystals

M. Rosen, S. Rucker, D. Caplan, and C. Schmidt

We have been using NMR to study the conformation and dynamics of molecules in anisotropic condensed phases. A system of particular interest is molecules dissolved in nematic liquid crystals, where reorientational motion is somewhat restricted. Two-dimensional, multiple-quantum NMR experiments on n-alkanes dissolved in nematic liquid crystals have been interpreted using simple models for molecular interactions. From these models we get a time-averaged picture of the conformation and orientation of the n-alkanes. We find that n-hexane is oriented to a significant extent by the liquid crystal and that it preferentially assumes elongated conformations (see Figure 10-1). We also find that n-octane is similar to n-hexane in that the end of an n-octane molecule behaves like an n-hexane molecule.

Figure 10-1. Conformations assumed by n-hexane in a liquid crystal solvent. (XBL 871-9525A)

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. T.P. Jarvie, K. Takegoshi, D. Suter, A. Pines, and D.B. Zax, "Suppression of the Zero-Frequency Peak in Time-Domain Zero-Field NMR," *Chem. Phys. Lett.* **158**, 325 (1989); LBL-24429.
2. J.W. Chang, C. Connor, E.L. Hahn, H. Huber, and A. Pines, "Direct Detection of Aluminum-27 Resonance with a SQUID Spectrometer," *J. Magn. Reson.* **82**, 387 (1989); LBL-26223.

3. N.Q. Fan, B. Heaney, J. Clarke, D. Newitt, L.L. Wald, E.L. Hahn, A. Bielecki, and A. Pines, "Nuclear Magnetic Resonance with dc SQUID Preamplifiers," *Proc. IEEE Trans. Mag.* **25**, 1193 (1989); LBL-26610.
4. H. Cho, K.T. Mueller, A.J. Shaka, and A. Pines, "Frequency Selective NMR Pulse Sequences Generated by Iterative Schemes with Multiple Fixed Points," *Mol. Phys.* **67**, 505 (1989); LBL-25943.
5. B.F. Chmelka, K.T. Mueller, A. Pines, J. Stebbins, Y. Wu, and J.W. Zwanziger, "Oxygen-17 NMR in Solids by Dynamic-Angle Spinning and Double Rotation," *Nature* **339**, 42 (1989); LBL-26732.
6. A. Samoson and A. Pines, "Double Rotor for NMR of Solids," *Rev. Sci. Instrum.* **60**, 3239 (1989); LBL-27251.
7. B.F. Chmelka and A. Pines, "Some Developments in Nuclear Magnetic Resonance of Solids," *Science* **246**, 71 (1989); LBL-27816.
8. J. Anandan and A. Pines, "Non-Abelian Geometric Phase from Incomplete Measurements," *Phys. Lett. A* **141**, 335 (1989); LBL-26532.
9. S.P. Rucker and A.J. Shaka, "Broadband Homonuclear Cross Polarization in 2D NMR Using DIPSI-2," *Mol. Phys.* **68**, 509 (1989); LBL-26611.
10. K.T. Mueller, B.Q. Sun, G.C. Chingas, J.W. Zwanziger, T. Terao, and A. Pines, "Dynamic Angle Spinning of Quadrupolar Nuclei," *J. Magn. Reson.* **86**, 470 (1990); LBL-27250.
11. L.C. de Menorval, D. Raftery, S.-B. Liu, K. Takegoshi, R. Ryoo, and A. Pines, "Investigations of Adsorbed Organic Molecules in NaY Zeolite by Xenon-129 NMR," *J. Phys. Chem.* **94**, 27 (1990); LBL-26371.
12. C. Connor, J.W. Chang, and A. Pines, "NQR and NMR Spectrometer with a dc SQUID Detector," *Rev. Sci. Instrum.* **61**, 1059 (1990); LBL-27255.
13. M. Gochin, A. Pines, M.E. Rosen, S.P. Rucker, and C. Schmidt, "Two-Dimensional NMR Studies of Flexible Molecules in Liquid Crystals: Orientational Order and Conformational Probabilities of *n*-Hexane," *Mol. Phys.* **69**, 671 (1990); LBL-27865.
- Stanford University, W. Little, Ed., World Scientific Press (in press); PUB-5261.
17. U. Werner, W. Müller-Warmuth, and A. Pines, "A Suggestion for Detecting Rotational Tunnelling of CD₃-Groups by Multiple-Quantum Spectroscopy," *Bull. Mag. Res.* (in press); LBL-28533.
18. D.N. Shykind, G.C. Chingas, A. Pines, and A.J. Shaka, "A Fast, Stable Quadrature Phase Generator for Multiple-Pulse NMR," *Rev. Sci. Instrum.* (in press); LBL-26372.
19. C. Connor, J.W. Chang, and A. Pines, "Direct Detection of Boron NQR using a dc SQUID," submitted to *J. Chem. Phys.*; LBL-27254.
20. S.-B. Liu, L.C. de Menorval, K. Takegoshi, R. Ryoo, M. Trecocke, and A. Pines, "Xenon-129 and Multiple-Quantum NMR Studies of Molecular Sorption in Na-Y Zeolite: The Effect of Thermal Treatment," submitted to *J. Phys. Chem.*; LBL-24425.
21. H. Cho, E.M. Scoffone, and A. Pines, "Composite Pulses with Dead Time Compensation for Broadband Excitation of Transverse Coherence in Solid State NMR," submitted to *J. Magn. Reson.*; LBL-27257.
22. K. Takegoshi, T.P. Jarvie, D. Suter, D.B. Zax, and A. Pines, "Spin-Echo Phenomena in Zero-Field NMR," submitted to *Chem. Phys.*; LBL-24426.
23. C.J. Lee, A. Samoson, B.Q. Sun, T. Terao, and A. Pines, "Possibility of Removing Second Order Broadening in NMR by Means of Sample Reorientation," *Proc. Nat. Acad. Sci.* (in press); LBL-25682.
24. G.C. Chingas, K. Mueller, B.Q. Sun, T. Terao, and A. Pines, "Avoiding Second Order Broadening by Flipping the Spinner Axis," *J. Magn. Reson.* (in press); LBL-25683.
25. K.T. Mueller, Y. Wu, B.F. Chmelka, J. Stebbins, and A. Pines, "The Use of Dynamic-Angle Spinning and Double Rotation in the Oxygen-17 NMR of Silicates," submitted to *J. Am. Chem. Soc.*; LBL-28534.
26. J.W. Zwanziger, M. Koenig, and A. Pines, "Non-Abelian Geometric Phase in a Quadrupole System Rotating Around Two Axes," submitted to *Phys. Rev. Lett.*; LBL-28535.
27. J.W. Zwanziger, M. Koenig, and A. Pines, "Berry's Phase," submitted to *Ann. Rev. Phys. Chem.*; LBL-28536.
28. C. Schmidt, D. Caplan, and M.F. Quinton, "Orientation and Motion of Tetrahydrofuran in Graphite Intercalation Compounds: ¹H NMR Spectra of Cs(THF)_{1.6}C₂₄ and K(THF)_{2.5}C₂₄," LBL-28537.
29. B.F. Chmelka, J.G. Pearson, S.B. Liu, M. Trecocke, and A. Pines, "Distributions of Aromatic Molecules in NaY Zeolite by Xenon-129 and Multiple-Quantum NMR," submitted to *J. Am. Chem. Soc.*; LBL-28538.
30. B.F. Chmelka, S.B. Liu, R. Csencsits, L.C. de Menorval, R. Ryoo, C.J. Radke, E.E. Petersen, and A. Pines, "Distribution of Platinum Guests in NaY Zeolite," submitted to *J. Catal.*; LBL-28539.
31. B.F. Chmelka, A.V. McCormick, L.C. de Menorval, and A. Pines, "Distribution of Xenon Atoms in NaA Zeolite," LBL-28540.
32. Y. Wu, B.F. Chmelka, M.E. Davis, P. Grobet, P. Jacobs, and A. Pines, "High resolution Aluminum-27 NMR of VPI-5, an

Other Publications

14. B.F. Chmelka, L.C. de Menorval, R. Csencsits, R. Ryoo, S.-B. Liu, C.J. Radke, E.E. Petersen, and A. Pines, "Calcination-Dependence of Platinum Cluster Formation in NaY Zeolite: A Xenon-129 NMR Study," in *Structure and Reactivity of Surfaces*, C. Morterra, A. Zecchina, and G. Costa, Eds., Elsevier Science Publishers, Amsterdam, 1989, p. 269; LBL-26609.

LBL Reports

15. A. Pines, "Abelian and Non-Abelian Holonomy in Magnetic Resonance Interferometry" in *Proc. Conf. Fundamental Aspects of Quantum Theory*, J. Anandan, Ed., World Scientific Press (in press); PUB-5262.
16. A. Pines, "NMR in Physics, Chemistry and Biology: Illustrations of Bloch's Legacy," in *Proc. Bloch Symposium*,

Aluminophosphate Molecular Sieve," submitted to Nature; LBL-28541.

33. Y. Wu, B.Q. Sun, A. Pines, A. Samoson, and E. Lippmaa, "NMR Experiments with a New Double Rotor," *J. Magn. Reson.* (in press); LBL-28542.
34. T.P. Jarvie (Ph.D. Thesis), "Molecular Structure and Motion in Zero Field Magnetic Resonance," LBL-28543.
35. C. Connor (Ph.D. Thesis), "Low Frequency Magnetic Resonance with a dc SQUID," LBL-28544.
36. B.F. Chmelka (Ph.D. Thesis), "Distribution of Metal and Adsorbed Guest Species in Zeolites," LBL-28545.

Invited Talks

37. A. Pines, "New Angles and Dimensions in NMR," Varian Technical Seminar Series, Palo Alto, CA, Jan. 16, 1989.
38. A. Pines, "There's No Free Induction," High Resolution NMR in Solids (symposium in honor of Professor John Waugh), Massachusetts Institute of Technology, Cambridge, MA, Jan. 19-21, 1989.
39. B.F. Chmelka, "Applications of Double Rotation NMR to Solid-State Materials Research," Basic Energy Sciences Laboratory Program Panel, MCSD, LBL, Jan. 26, 1989.
40. A. Pines, "High Resolution Solid State NMR," Korea Institute of Science and Technology, Seoul, Republic of Korea, Jan. 25, 1989.
41. A. Pines, "Two-Dimensional NMR and Molecular Conformations," Taedak Science Town, Republic of Korea, Jan. 26, 1989.
42. A. Pines, "High-Resolution Solid State NMR," Pohang Institute of Technology, Pohang, Republic of Korea, Jan. 27, 1989.
43. A. Pines, "High-Resolution Solid State NMR," "Multiple-Quantum NMR Spectroscopy—I," "Multiple-Quantum Spectroscopy—II," "Zero-Field NMR and SQUID-NMR," and "Quantum Phase and Topology," Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Republic of China, Jan. 30, 1989.
44. A. Pines, "Two Dimensional NMR and Molecular Conformation in Liquid Crystals," National Tsing-Hua University, Republic of China, Feb. 1, 1989.
45. A. Pines, "Berry's Phase for Bloom and Other Vegetables," Department of Physics, University of British Columbia, Feb. 23, 1989.
46. A. Pines, "Making NMR 'Count'," "Advances in Chemistry" series, Department of Chemistry, University of Houston, Houston, TX, Feb. 28, 1989.
47. A. Pines, "Recent Development in NMR at Berkeley," Chemistry Department, Rice University, Houston, TX, Mar. 1, 1989.
48. A. Pines, "Magic and Other Angles in NMR Spectroscopy," Chemistry Department, University of Texas at Austin, Mar. 2, 1989.
49. C. Schmidt, "Two-Dimensional NMR and Mean-Field Models of Hydrocarbon Chains in Liquid Crystals," VI. European Liquid Crystal Winter Conference, Schladming, Austria, Mar. 5-10, 1989.
50. A. Pines, "There's No Free Induction: Some Recent Developments in Pulsed NMR," Spectroscopy Society of Pittsburgh Award Lecture, Pittsburgh Conference and Exposition, Atlanta, GA, Mar. 8, 1989.
51. J.W. Zwanziger, "NMR in the Solid State—New Experiments and Theory Using Sample Reorientations," Department of Chemistry, Indiana University, Bloomington, Mar. 1989.
52. B.F. Chmelka, "Distributions of Organic Adsorbates in NaY," Molecular Thermodynamics Research Seminar, University of California at Berkeley, Mar. 29, 1989.
53. A. Pines, "Recent Developments in NMR at Berkeley," Lockheed Colloquium Series, Palo Alto Research Laboratories, Palo Alto, CA, Mar. 30, 1989.
54. A. Pines, "New Angles in Sample Spinning," 30th Experimental Nuclear Magnetic Resonance Conference, Asilomar, CA, Apr. 2-6, 1989.
55. A. Pines, "Novel NMR Detection Schemes," 30th Experimental Nuclear Magnetic Resonance Conference, Asilomar, CA, Apr. 2-6, 1989.
56. B.F. Chmelka, "Distributions of Metals and Adsorbed Guests in Zeolites," Mobil Research and Development Corp., Paulsboro, NJ, April 1989.
57. A. Pines, "There's No Free Induction," 11th Graduate Student Symposium, University of Rhode Island, Kingston, Apr. 29, 1989.
58. A. Pines, "NMR Concepts," Trafficante Series, University of Rhode Island, Kingston, May 1, 1989.
59. A. Pines, "Novel NMR Detection Schemes," Analytical Division, Chemistry Department, Ohio State University, Columbus, May 2, 1989.
60. A. Pines, "Quantum Measurement," Miller Institute, University of California at Berkeley, May 9, 1989.
61. A. Pines, "Berry's Phase" and "Multiple-Quantum Spectroscopy," 11th Waterloo Summer Institute Advances in NMR, Waterloo, Ont., June 12-16, 1989.
62. A. Pines, "Magic and Other Angles," Gordon Conference on Magnetic Resonance, Plymouth, NH, June 19-23, 1989.
63. B.F. Chmelka, "Double Rotation and Dynamic-Angle Spinning NMR," Max-Planck-Institut für Medizinische Forschung, Heidelberg, Federal Republic of Germany, July 5, 1989; Max-Planck-Institut für Polymerforschung, Mainz, Federal Republic of Germany, July 7, 1989.
64. A. Pines, "Multiple-Quantum NMR Studies of Hydrocarbon Chain Conformations," 9th Specialized Colloque Ampere "Magnetic Resonance in Polymers," Prague, Czechoslovakia, July 10-13, 1989.
65. A. Pines, "SQUID Detection of Magnetic Resonance: Results and Prospects," 10th ISMAR Conference, Morzine, France, July 16-21, 1989.
66. A. Pines, "Zero Field Magnetic Resonance at Berkeley," Xth International Symposium on Nuclear Quadrupole Resonance Spectroscopy, Takayama, Japan, Aug. 22-26, 1989.
67. J.W. Zwanziger (speaker), B.F. Chmelka, K.T. Mueller, A. Pines, A. Samoson, J. Stebbins, and Y. Wu, "Resolution of Similar Quadrupolar Sites in NMR Spectra of Solids," Fifth

- International Symposium on Magnetic Resonance in Colloid and Interface Science, Newark, DE, Aug. 1989.
68. A. Pines, "Recent Development in NMR at Berkeley," 6th German-Israeli Gertner-Minerva Symposium in Chemistry, Weizmann Institute of Science, Eilat, Israel, Sept. 24-28, 1989.
 69. A. Pines, "Geometric Quantum Phase for Protons and Photons," MSI Workshop on Geometric Phases in Mechanics, Mathematical Sciences Research Institute, Cornell University, Ithaca, NY, Oct. 9-13, 1989.
 70. J.W. Zwanziger (speaker), M. Koenig, and A. Pines, "Experimental Measurement of Geometric Phases: the Non-Abelian Case," MSI Workshop on Geometric Phases in Mechanics, Mathematical Sciences Research Institute, Cornell University, Ithaca, NY, Oct. 9-13, 1989.
 71. A. Pines, "Nuclear Magnetic Resonance in Physics, Chemistry and Biology," Bloch Symposium, Stanford University, Stanford, CA, Oct. 27-28, 1989.
 72. A. Pines, "Mending the Symmetry in NMR," Chemistry Department Lecture, Dalhousie University, Halifax, NS, Nov. 6, 1989.
 73. A. Pines, "Irreversibility?" Walter J. Chute Lecture, Department of Chemistry, Dalhousie University, Halifax, NS, Nov. 7, 1989.
 74. A. Pines, "Magnetic Moments," C.A. McDowell Lecture, Department of Chemistry, University of British Columbia, Vancouver, Nov. 14, 1989.
 75. A. Pines, "Magic and Other Angles in NMR Spectroscopy," Department of Chemistry, University of British Columbia, Vancouver, Nov. 15, 1989.
 76. A.V. McCormick (speaker), B.F. Chmelka, and A. Pines, "Interactions Inside a Micropore as Studied by ^{129}Xe NMR with NaA Zeolites," American Institute of Chemical Engineers National Meeting, San Francisco, CA, Nov. 1989.
 77. A. Pines, "Solid State NMR and the Icosahedron," Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Nov. 30, 1989.
 78. A. Pines, "Nonabelian Holonomy in NMR Interferometry," Conference on Fundamental Aspects of Quantum Theory to Celebrate 30 Years of the Aharonov-Bohm Effect, University of South Carolina, Columbia, Dec. 14-16, 1989.
 79. A. Pines, "Some New Developments in NMR of Quadripolar Nuclei," Symposium on Analytical Applications of Solid-State NMR, International Chemical Congress of Pacific Basin Societies, Honolulu, HI, Dec. 17-22, 1989.

Synthesis of Novel Solids*

Angelica M. Stacy, Investigator

INTRODUCTION

The goal of this research is to synthesize advanced materials with novel properties. Current work is focused on rare-earth transition-metal phosphides. Rare-earth compounds have attracted attention because they exhibit cooperative phenomena, including valence fluctuations, heavy-fermion superconductivity, and unusual types of magnetic ordering. These cooperative phenomena are difficult to model and remain a challenge to our understanding of condensed matter. The goals are to synthesize and characterize new classes of rare-earth transition-metal phosphides that exhibit cooperative phenomena (especially superconductivity). Such synthetic studies will lead to numerous new classes of materials with novel magnetic and electronic properties.

1. Work in Progress

Since the publication of the first two papers on EuNi_5P_3 describing its structure and magnetic properties, this group has obtained resistivity data, heat-capacity measurements, and preliminary neutron-diffraction data on EuNi_5P_3 , and magnetic measurements on Ca- and Sr-doped materials.

Single crystals of EuNi_5P_3 suitable for single-crystal neutron-diffraction experiments have been obtained both by melt growth and by growth in a tin flux. These samples have been carefully analyzed by Laue back-reflection x-ray diffraction to verify that they are indeed single crystals. This procedure was not trivial, as the Laue back-reflection patterns obtained are quite complex and therefore difficult to interpret. It was necessary to write a computer program to generate idealized patterns; the fact that the calculated patterns were identical to those obtained experimentally indicates the high quality of the crystals obtained.

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A study of fluctuating valence in EuNi_2P_2 was undertaken. EuNi_2P_2 is of interest because the oxidation state of the Eu atoms is between +2 and +3, yet the Eu atoms in the compound are indistinguishable. In contrast, although EuCo_2P_2 is isotypic with EuNi_2P_2 , the Eu atoms in EuCo_2P_2 are in the +2 oxidation state. In order to better understand the important parameters relating to the phenomenon of fluctuating valence, solid solutions of intermediate composition $\text{EuCo}_{2-x}\text{Ni}_x\text{P}_2$ were prepared and characterized. In the course of this study, a new compound, EuCoNiP_2 , was discovered.

Synthesis of the $\text{EuCo}_{2-x}\text{Ni}_x\text{P}_2$ materials has been adapted from the reported synthesis of EuCo_2P_2 and EuNi_2P_2 in a tin flux. The synthesis of $\text{EuCo}_{2-x}\text{Ni}_x\text{P}_2$ materials was attempted for starting compositions of $x = 0.5, 1.0$, and 1.5 . Structural characterization was performed by x-ray powder diffraction and energy-dispersive spectroscopy (EDS). Characterization of magnetic behavior was carried out by magnetization measurements at various fields and temperatures. Single-phase materials have been successfully synthesized and characterized for $x = 0.5$ and 1.5 . The changes in structure and magnetic behavior in these two materials can be understood as systematic perturbations from the unsubstituted materials.

The attempt to synthesize $\text{EuCo}_{2-x}\text{Ni}_x\text{P}_2$ for $x = 1.0$ in the tin flux has produced an unanticipated result. The product consisted of two phases, suggesting a phase separation due to electronic and structural requirements that the $x = 1.0$ composition does not satisfy. Different synthetic approaches to the material at $x = 1.0$ have been attempted, and characterization has indicated that a single-phase material has been prepared. However, this material, of composition EuCoNiP_2 , does not appear to be isostructural with either end member. Further studies to elucidate the structure of this new compound remain to be pursued.

1989 PUBLICATIONS AND REPORTS

Other Publications

1. J.V. Badding and A.M. Stacy, "Synthesis and Crystal Structure of a New Alkaline Earth Nickel Phosphide: BaNi_9P_5 ," submitted to J. Solid State Chem.
2. J.V. Badding (Ph.D. Thesis), "An Unusual Series of Magnetic Phase Transitions in EuNi_5P_3 ."

Studies of the Metal/Solution Interface with X Rays*

Philip N. Ross, Investigator

INTRODUCTION

During the last two decades there have been great advances in the development of methods for the analysis of the structure of surfaces in ultrahigh vacuum (UHV), which has led to a detailed understanding of the chemistry of free surfaces. Further advances of comparable magnitude will be necessary to develop an equivalent level of understanding of structures at interfaces, particularly the technologically important cases of interfaces between condensed phases. In this work, we address the problem of structure determination at the metal/solution interface. Study of the metal/solution interface is relevant to technologies like metal corrosion, electrochemical energy conversion (fuel cells), and storage devices (batteries) and the rapidly growing new technology of electrolytic epilayers for photovoltaics, magnetic recording, and electro-optic devices.

The problem of structure determination at the interface between condensed phases is a difficult one. Most of the techniques developed for the study of solid surfaces in UHV cannot be applied to the interface between condensed phases, since they rely on the diffraction, scattering, or emission of electrons. The electrons scattered or emitted from the interface are too severely attenuated by the condensed phases for external detection and analysis. New techniques must be developed that utilize more penetrating, higher-momentum photons like x rays, gamma rays, or neutrons. We are pursuing the use of x rays, and especially x-ray diffraction, for structure determination at the metal/solution interface.

In recent years there have been several approaches to the development of surface-sensitive x-ray diffraction, including x-ray standing waves, direct-transmission diffraction from thin substrates, and grazing-incidence Bragg diffraction at the critical angle for total reflection (GID). The grazing-incidence geometry appears to be the most generally applicable technique for our purposes. GID is a very new surface tool that has been used only a few times, for some solid/solid interfaces (multilayers) and submonolayer metal/metal surfaces in UHV. Prior to this study, the application of GID to a solid/liquid interface was a totally new experiment.

1. Work in Progress

The reconstruction of the Au(111) and (100) surfaces at potentials cathodic to the potential of zero charge (PZC) into structures that appear to be related to the UHV reconstructions are being studied in detail using both x-ray reflectivity measurements and GID. The type of cation in the electrolyte, and the chemistry of the ion-metal interaction, are expected to play an important role in the reconstruction. Also of interest here are other metals whose clean low-index surfaces are not reconstructed in UHV but become reconstructed when alkali metals are placed on the surface, such as the (1×2) reconstructions of Ag(110), Pd(110), and Cu(110) caused by K adsorption. Such reconstructions may also occur on these surfaces at potentials cathodic to their PZCs in potassium-containing electrolyte, depending on the effect of solvation on the alkali metal/noble metal interaction; i.e., reconstruction may occur only in electrolytes with weakly solvated cations like Cs.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. P.N. Ross, "Single Crystal Electrochemistry: Experimental Challenges to Current Theory," *Electrochim. Acta* **34**, 1897 (1989).
2. J. Kortright, P. Ross, O. Melroy, M. Toney, G. Borges, and M. Samant, "Electrochemically Adsorbed Pb on Ag(111) Studied with GIXS," *J. de Physique C7*, 153 (1989); LBL-24454.

*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-7SF00098.

Interfacial Materials and Processes*

John D. Porter, Investigator

INTRODUCTION

Fundamental research into the structure, properties, and dynamics of interfacial systems is performed. The objective of this program is to obtain physical and chemical information about interfaces at the molecular level, using experimental techniques that can be applied *in situ*. At the core of the program are studies of scientifically and technologically relevant interfaces formed between dielectrically dissimilar materials, such as metal/insulator, metal/semiconductor, and semiconductor/insulator interfaces. The emphasis is on the study of experimentally challenging systems that contain a liquid component. Model systems are synthesized and used to critically test theory and to develop new interface characterization techniques. Novel high-resolution, *in situ* experimental methods are being developed that use electrons as direct structural and spectroscopic probes.

1. Work in Progress

The technology for preparing atomically smooth large-area metal/liquid/metal (M/L/M) tunnel-junction devices was refined. Using these devices, the dynamic structuring and properties of liquid water at Hg/H₂O interfaces was studied in detail. It was found that water structuring is dynamic but ice-like at the interface. A wider variety of "layered" configurations was observed than is usually postulated to occur at metal surfaces. There appears to be no single preferred orientation of water at mercury surfaces in the absence of an external electric field. Structuring at the interface appears to extend for up to two to three layers into the liquid. Dielectric saturation and dispersion was observed in the first few water layers.

Preliminary results were obtained for other dielectric liquids using M/L/M junction devices. Interfacial structuring of liquid methanol and carbon tetrachloride was also observed at mercury surfaces, and results are presently

being analyzed. In other experiments, compound structures were made by chemisorbing small molecules to the metal surfaces, and the properties of Hg/spacer/H₂O/spacer/Hg junctions were determined. The exciting result was that junction properties were sensitive to the orientation of the small spacer molecules on the metal surface.

Photoemission and direct collection of electrons was performed in a condensed medium for the first time using M/L/M junction devices. The method was used to obtain an independent measure of the position of the conduction band edge of liquid water at the Hg/H₂O interface. In the past, studies of photoemission into condensed media have been complicated tremendously by the scattering, trapping, and subsequent chemical reactions of the emitted electrons. The M/L/M device geometry allowed us to generate and collect ballistic electrons because the interelectrode spacing was smaller than the thermalizing lengths.

Work continues on the study of surface diffusion of silver adatoms at ideal Ag(111)/H₂O interfaces. Improvements in our methods were combined with modeling and simulation studies of this process. We find D_s values near 1×10^{-7} cm²/sec at room temperature. This is about 18 times smaller than values predicted for surface self-diffusion in ultrahigh vacuum (UHV). Temperature dependences of the surface self-diffusion coefficient indicate that steric crowding by adsorbed water raises the activation energy for diffusion by about 50% compared to the free-surface UHV, while the pre-exponential factor is about 35% smaller. We conclude that silver adatoms diffuse interstitially through adsorbed water and do not displace water at the interface.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. P.B. Price, S.W. Barwick, W.T. Williams, and J.D. Porter, "Search for Energetic Charged Particles from Deuterated Pd and Ti Foils," *Phys. Rev. Lett.* **63**, 1926 (1989).

LBL Reports

2. J.D. Porter, A.A. Shahab-Eldin, H. Boney, F.J. Echegaray, J.M. Nyschke, S.G. Prussin, J.O. Rasmussen, and M.A. Stoyer, "Limits on Electromagnetic and Particle Emission for Palladium D₂O Electrolytic Cells," *J. Fusion Energy*, in press (LBL 27521).

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Chemical
Sciences

FUNDAMENTAL INTERACTIONS

PHOTOCHEMICAL AND RADIATION SCIENCES

Photochemistry of Materials in the Stratosphere*

Harold S. Johnston, Investigator

INTRODUCTION

This research is concerned with global change in the atmosphere, including photochemical modeling and experimental gas-phase photochemistry. In collaboration with Lawrence Livermore National Laboratory, theoretical studies are made of atmospheric transport, radiation balance, and photochemistry. One goal of the experimental work is to obtain optical and kinetic data in the laboratory that are needed by modelers of the atmosphere. Another goal is to study molecular dynamics. The experimental methods include laser flash photolysis, laser resonance absorption, resonance fluorescence, and dispersed chemiluminescence from photolysis products.

1. Nitrogen Dioxide Fluorescence Lifetimes over a Wide Range of Excitation Wavelengths (Publication 4)

K.O. Patten, Jr., J.D. Burley, and H.S. Johnston

The fluorescence of nitrogen dioxide excited by a pulsed, tunable dye laser was measured in a large flask at low pressures and short times to obtain the zero pressure radiative lifetime from 400 to 750 nm. In general, these lifetimes agree with, and extend the range of, recent values in the literature. Collisional quenching rate constants between excited nitrogen dioxide and ground-state molecules were obtained over the same range of conditions; and a clear understanding was obtained that these measurements, like most other measurements of this kind in the literature, depend so seriously on experimental conditions that they have little significance. A new experimental method has been developed to overcome most

of these difficulties and to obtain extensive, fundamental data on collisional deactivation of highly excited nitrogen dioxide molecules.

2. Calibration of the LLNL Two-Dimensional Atmospheric Model (Publication 5)

D. Kinnison

In collaboration with scientists at Lawrence Livermore National Laboratory (LLNL), the LLNL two-dimensional chemical-radiative-transport model of the global atmosphere has been tested against the (AEC) observed excess carbon-14 from the nuclear-bomb tests of 1961-1962, covering the period from 1962 to 1970 (compare Publication 1).

Although the carbon-14 observations were over only limited regions of the stratosphere, the LLNL model was in good agreement with observations over the full 8-year period.

3. *Ab Initio* Study of the Vibrational Spectra of NO₃ (Publication 6)

B. Kim, B.L. Hammond, W.A. Lester, Jr., and H.S. Johnston

As an ozone-destroying catalyst in the lower stratosphere and a night-time oxidant in the troposphere, the nitrate free radical is a moderately important atmospheric species. The vibrational spectra and geometry of the NO₃ molecule have been studied using *ab initio* self-consistent field (SCF) and complete-active-space SCF methods. For all levels of theory and basis set, the highest symmetry found is C_{2v}.

4. Work in Progress

A simple pulsed molecular-beam machine has been constructed and used to study collision-free, photolysis-induced fluorescence of nitrogen dioxide. Photolysis-induced fluorescence of nitrogen dioxide and laser-induced fluorescence of nitrogen dioxide have been found here to give molecular populations of highly excited internal energy states. By use of the method derived here in recent years to study photolysis-induced fluorescence, the

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first four moments of the internal energy distribution of highly excited NO₂ molecules have been evaluated as a function of collision number. These experiments give an unusually large amount of information about energy-transfer processes. With the strong connections established between this project and the Atmospheric Sciences group at LLNL, extensive further calculations are planned concerning global budgets of ozone, oxides of nitrogen, chlorine compounds, heterogeneous chemistry in the stratosphere, the effects of stratospheric aircraft, and related problems.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. H. Johnston, "Use of Excess Carbon-14 Data to Test Two-Dimensional Stratospheric Models," *J. Geophys. Res.* **94**, 18485 (1989); LBL-25677.

2. H. Johnston, D. Kinnison, and D. Wuebbles, "Nitrogen Oxides from High Altitude Aircraft: An Update of Potential Effects on Ozone," *J. Geophys. Res.* **94**, 16351 (1989); LBL-26206.
3. D. Darwin, A. Young, H. Johnston, and C.B. Moore, "Rate Constants for $\text{C}_2\text{H}_2(\text{X}^3\text{B}_1)$ Removal by O₂, NO, and C₂H₂ from Infrared Diode Laser Flash Kinetic Spectroscopy," *J. Phys. Chem.* **93**, 1074 (1989); LBL-25112.

LBL Reports

4. K.O. Patten, Jr., J.D. Burley, and H.S. Johnston, "Radiative Lifetimes of Nitrogen Dioxide for Excitation Wavelengths from 400 to 750 nm," submitted to *J. Phys. Chem.*; LBL-28435.
5. D.E. Kinnison (Ph.D. Thesis), "Effects of Trace Gases on Global Atmospheric Chemical and Physical Processes," LBL-28439.
6. B. Kim, B.L. Hammond, W.A. Lester, Jr., and H.S. Johnston, "*Ab Initio* Study of the Vibrational Spectra of NO₃," submitted to *Chem. Phys. Lett.*; LBL-28434.

CHEMICAL PHYSICS

Energy Transfer and Structural Studies of Molecules on Surfaces*

Charles B. Harris, Investigator

INTRODUCTION

The goal of this research is to study the mechanisms that are responsible for the transfer of energy from the excited states of molecules to metal surfaces and to develop new laser techniques for probing molecule-surface interactions. The research program is both theoretical and experimental in character and includes nonlinear optical, picosecond, and femtosecond laser techniques in addition to a variety of standard surface-science tools for characterizing molecule-surface interactions. Recent work has centered on the development of picosecond infrared lasers; the elucidation of the mechanisms of surface-enhanced photochemistry, surface-enhanced photoelectron emission, and the breakdown of classical dielectric response theory for explaining energy transfer from molecules to noble-metal surfaces; and the development of new techniques for studying the dynamics of electrons at interfaces on femtosecond timescales. The results of this program have a direct bearing on high-speed technological devices and materials, and on other problems of general interest such as the dynamics of electrical transmission in conductors on ultrafast timescales and the optical properties of thin films.

1. Time-Resolved Luminescence of Electron-Hole Pair in $\text{CdS}_x\text{Se}_{1-x}$ Graded Semiconductors (Publication 1)

C.B. Harris

Time-resolved photoluminescence (PL) from graded $\text{CdS}_x\text{Se}_{1-x}$ samples that exhibit spatially resolved PL has been used to study the dynamics of nonequilibrium

distributions of electron-hole pairs in air at 295 K. The samples, which possess graded zones spanning roughly the entire alloy compositional range in a thickness of $\sim 1 \mu\text{m}$, have been prepared with the band gap increasing both toward the surface (CdSe/S) and toward the bulk (CdS/Se). Decay times ($1/\tau$) in PL spectra for CdS/Se and CdSe/S samples, measured between ~ 500 and 740 nm (corresponding to edge emission from the $\text{CdS}_x\text{Se}_{1-x}$ alloy compositions comprising the graded zones), occur over roughly $100\text{--}400 \text{ psec}$ and are strongly dependent on detection wavelength, reflecting carrier dynamics. The decay traces show a nonmonotonic dependence on detection wavelength.

2. A New Technique for the Determination of Surface Adsorbate Geometries Utilizing Second Harmonic Generation and Adsorption Band Shifts (Publication 2)

C.B. Harris

A combination of second harmonic generation (SHG) and a simple dipole-dipole interaction model is presented as a new technique for determining adsorbate geometries on surfaces. The polarization dependence of SHG is used to define possible geometries of the adsorbate about the surface normal (see Figure 2-1). General formulae for absorption band shifts using the geometry constraints imposed by the SHG data are derived for a dimer constructed from two arbitrarily placed monomers on the surface using the dipole-dipole interaction potential. These formulae can be used to determine the orientation of the two monomers relative to each other. A simplified version of this formalism is used to interpret absorption band shifts for a system of rhodamine B adsorbed on quartz.

3. Work in Progress

Picosecond transient absorption studies were carried out for the photodissociation of $\text{Cr}(\text{CO})_6$ in cyclohexane, THF, and chlorinated methanes, and of $\text{M}_2(\text{CO})_{10}$ ($\text{M} = \text{Mn}$ and Re) in hydrocarbon solvents. The rise and decay of transient signals depended on solvents as well as on the probe wavelength in the region of 450 to 680 nm . The decay kinetics are examined in terms of vibrational cooling,

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Figure 2-1. Possible dimer geometries (omitting the amino and carboxyl groups for clarity). (XBL 892-635)

solvation, and geminate recombination, and a model is proposed to describe the experimental observations.

The A/A state lifetime of I_2 in various deuterated hydrocarbon solvents has been determined from picosecond transient absorption spectra. The lifetime observed in the deuterated on solvents is 2.0 times as long as that measured in the corresponding undeuterated solvent. A mechanism involving energy transfer through solvent-solute complex vibrational modes is proposed to explain this effect and the overall trend of shorter lifetime with increasing solvent hydrogen concentration.

A comprehensive method to study the ultrafast dynamics of electrons at surfaces using angle-resolved photoemission, thermomodulation spectroscopy, and femtosecond laser pump-probe techniques has been developed. The results will help clarify the mechanisms of optical damage and surface melting and may lead to methods of controlling them.

Understanding the dynamics of the basic processes associated with the interaction between intense laser beams and surfaces is important to optical-damage investigations, optoelectronics, and laser processing of materials. To gain a basic understanding of the ultrafast dynamics of electrons on surfaces, a comprehensive method for studying electron dynamics and time-dependent behavior at surfaces on ultrafast time scales using a combination of angle-resolved photoemission, thermomodulation spectroscopy, and

femtosecond laser pump-probe techniques has been developed.

When light interacts with a metal, energy is first absorbed by conduction electrons that thermalize via electron-electron scattering and then transfer their energy to the crystal lattice through electron-phonon coupling. These processes occur within tens and hundreds of femtoseconds, respectively. Using a 310-nm pump pulse, electrons are excited from bulk states and occupied surface states on metals to empty image-potential states above the Fermi level but below the vacuum level. To follow the dynamics of electrons in these states, the electrons are photoionized out of the states using a variably delayed 620-nm probe pulse. The energy and momentum distribution of electrons emitted from the surface are then determined via their angle-resolved time of flight. This detection system can process several events per laser pulse at a high repetition rate (8 kHz) without space-charge broadening effects. One can thus collect 10^4 to 10^5 e/s with an energy resolution of about 20 meV and a time resolution limited only by laser pulse length. Preliminary two-photon photoemission spectra from Cu(100) with ultraviolet pulses show the lowest-lying image potential state at 3.8 eV, which is consistent with previously reported results.

Electron-phonon coupling was measured simultaneously using transient thermomodulation spectroscopy, which monitors the change in reflectivity of the light from the sample caused by the change in the dielectric constants of the material as it is heated.

Initial experiments concentrated on electron-electron interactions decoupled from bulk processes to characterize these diagnostics. Now the dynamics of electrons in image-potential states on the Cu(100) surface are being investigated to determine the decay mechanisms for excited surface electrons.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. J.K. Hane, M.G. Prisant, C.B. Harris, G.J. Meyer, L.K. Leung, and A.B. Ellis, "Time-Resolved Luminescence of Electron-Hole Pairs in CdS_xSe_{1-x} Graded Semiconductors," *J. Phys. Chem.* **93**, 7975 (1989); LBL-26764.
2. E.S. Peterson and C.B. Harris, "A New Technique for the Determination of Surface Adsorbate Geometries Utilizing Second Harmonic Generation and Absorption Band Shifts," *J. Chem. Phys.* **91**, 2683 (1989); LBL-26765.

LBL Reports

3. M.E. Paige and C.B. Harris, "Effects of Solvent-Solute Complexation on Barrier Crossing," submitted to *J. Chem. Phys. Notes*; LBL-28553.[†]
4. M. Lee and C.B. Harris, "Ultrafast Studies of Transition Metal Carbonyl Reactions in Condensed Phase: Cooling and Solvation of Photoproducts," submitted to *J. Am. Chem. Soc.*; LBL-28563.[†]
5. D.E. Smith (Ph.D. Thesis), "Studies of Simple Chemical Reactions in Solution: Iodine Photodissociation, Recombination, and Relaxation and the Development of Autoregressive Procedures for Application to Stochastic Simulations," LBL-27795.[‡]

Invited Talks

6. C.B. Harris, "Dynamical Processes in Condensed Phase on Ultrafast Timescales," Workshop on Chemical Reaction Dynamics, Berkeley Conference Center, Berkeley, CA, Nov. 2, 1988.
7. C.B. Harris, "Reaction Dynamics in Liquids and Electron-Hole Pair Dynamics in Graded Semiconductors," Sandia National Laboratory, Livermore, CA, Nov. 11, 1988.
8. C.B. Harris, "Dynamical Processes in Condensed Phase on Ultrafast Timescales," Argonne National Laboratory, Argonne, IL, Nov. 28, 1988.
9. C.B. Harris, "Applications of Parametric Analysis and Covariant Sequences to Dynamical Processes in Condensed

- Phase on Ultrafast Time Scales," International Conference on Lasers '88, Lake Tahoe, NV, Dec. 5-9, 1988.
10. C.B. Harris, "Fundamental Studies of Bond Breaking and Forming on Ultrafast Timescales," Energetic Materials Initiation Fundamentals meeting, Sandia National Laboratory, Livermore, CA, Dec. 9, 1988.
11. C.B. Harris, symposium on Photochemistry in Thin Films, SPIE, Los Angeles, CA, Jan. 15-20, 1989.
12. C.B. Harris, "Fundamental Studies of Bond Breaking and Forming on Ultrafast Timescales," IBM, San Jose, CA, Feb. 9, 1989.
13. C.B. Harris, organized American Physical Society symposium on Reaction Dynamics in Liquids on Ultrafast Timescale, St. Louis, MO, Mar. 20-24, 1989.
14. C.B. Harris, "Dynamical Processes in Condensed Phase on Ultrafast Timescales," ACS meeting on Relaxation and Dynamics in Complex Media, Dallas, TX, Apr. 9-14, 1989.
15. C.B. Harris, "Fundamental Studies of Bond Breaking and Forming on Ultrafast Timescales," Fourth International Conference on Time Resolved Vibrational Spectroscopy, Princeton, NJ, June 11-15, 1989.
16. C.B. Harris, "The Role of Vibrational Redistribution and Relaxation in Chemical Reactions in Liquids on Ultrafast Timescales," Femtosecond Chemistry Symposium, American Chemical Society, Miami, FL, Sept. 10-15, 1989.

[†]Office of Naval Research Program using DOE equipment.

[‡]National Science Foundation Program using DOE equipment.

Selective Photochemistry*

C. Bradley Moore, Investigator

INTRODUCTION

The fundamental goal of this program is to understand the photophysics and photochemistry that occur following selective excitation of molecules and during the reactions of free radicals. Of particular interest are the chemical reactions of specifically excited states and the dynamics of energy transfer, both within a molecule and to surrounding molecules.

Molecules produced in bound excited singlet states may fragment following the conversion of electronic excitation energy into vibrational energy. Intersystem crossing to triplet states is often in competition with internal conversion to singlet states. In this work the dynamics of intersystem crossing and reaction of the triplet state are studied for both unimolecular and bimolecular systems.

For low levels of vibrational excitation in small molecules, individual quantum states may be excited, enabling the measurement of reaction and energy-transfer rate constants for each quantum state. For larger or more highly excited molecules, it is usually not possible to excite single eigenstates. Instead, a number of eigenstates are excited simultaneously, and a redistribution of the initial vibrational excitation occurs. This process, known as intramolecular vibrational-energy redistribution (IVR), is extremely rapid and severely limits the realization of truly mode-specific unimolecular reactions. Advances in mode-specific chemistry will come from a more complete understanding of the IVR process and the parameters that control its efficiency. By being able to predict the rates of IVR and the path of vibrational-energy flow through a molecule, experiments can be designed utilizing molecular systems that maximize the possibilities for mode-specific effects. Studies designed to elucidate the coupling mechanisms and dominant pathways for IVR are currently under way on a number of model systems.

The rates and mechanisms of free-radical reactions, such as are important in combustion, are often best studied by flash kinetic spectroscopy using lasers for thermal heating, for photolyzing, and for spectroscopic probing. Reactions can be studied as a function of individual quantum states. A fundamental understanding of the rate

constants and product distributions for these reactions is sought to serve as a basis for modeling combustion processes.

1. Photofragmentation of Ketene to $\text{CH}_2(\tilde{X}^3\text{B}_1) + \text{CO}$: I. Barrier Height And Dissociation Rate Constant (Publication 3)

I-C. Chen and C.B. Moore

Ketene cooled in a supersonic free jet is photolyzed in the ultraviolet range. The appearance rate of fragment CO from triplet ketene as a function of ultraviolet photon energy is measured by vacuum ultraviolet laser-induced fluorescence. A tunneling-corrected RRKM theory is used to fit the observed dissociation rate of ketene using the *ab initio* vibrational frequencies of the transition state. The density of states inferred from the RRKM fit is a factor of 2 greater than the density of states of the ground electronic state (S_0) and 300 times greater than that of T_1 . Tunneling corrections are necessary to fit the dissociation rate below the top of the exit barrier. The experimental rates show a sharp change in slope at $28,290\text{ cm}^{-1}$ photolysis frequency. The height of the exit barrier is determined to be $3.79 \pm 0.06\text{ kcal/mol}$ above ground-state fragments. The imaginary frequency that fits the data is $(150 \pm 25)i\text{ cm}^{-1}$, much lower than the *ab initio* frequency of $523i\text{ cm}^{-1}$. At higher energies, the RRKM theory predicts faster rates than are observed. It is possible that the intersystem crossing rate is relatively independent of energy and becomes the rate-determining step for formation of triplet products at higher energies.

2. Photofragmentation of Ketene to $\text{CH}_2(\tilde{X}^3\text{B}_1) + \text{CO}$: II. Rotational State Distributions of Product CO (Publication 4)

I-C. Chen and C.B. Moore

Ketene cooled in a supersonic jet is photolyzed at 1120 , 190 , and 30 cm^{-1} above and at 50 cm^{-1} below the top of the barrier to dissociation on the triplet surface. The barrier is 1330 cm^{-1} above $\text{CH}_2(\tilde{X}^3\text{B}_1) + \text{CO}$. The rotational-state distributions of CO produced from triplet ketene are measured using vacuum UV laser-induced fluorescence. These distributions can not be described adequately by a Boltzmann temperature or by phase-space statistical models. An average of $22.4 \pm 1\%$ of the total available energy goes to CO rotation, as predicted by an impulsive model using the *ab initio* transition-state geometry. This result indicates that the energy partitioning is determined by the geometry of the transition state with

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the repulsive force directed along the breaking bond. The fraction of energy going to CO rotation does not depend on the photolysis wavelength. The Gaussian shape of the CO rotational-state distribution can be understood quantitatively in terms of the zero-point motion of the C-C-O bending vibration of the transition state. Even when the excess energy above the top of the barrier is comparable to the barrier height itself, the energy release appears to be completely dynamically controlled.

3. Vibrational Photochemistry of Porphine Imbedded in an n-Hexane-d₁₄ Shpol'skii Matrix (Publication 6)

T.J. Butenhoff, R.S. Chuck, H.-H. Limbach, and C.B. Moore

The near infrared-induced tautomerization of free-base porphine incorporated in an n-hexane-d₁₄ matrix is reported. Porphine occupies two sites in an n-hexane-d₁₄ matrix, as opposed to one site in an n-hexane matrix. Two spectroscopically distinct tautomers, differing by a 90° rotation of the NH bond axes within the molecular plane, exist for each site. Nernst glower irradiation on the NH stretch fundamental does not induce tautomerization, but irradiation in the regions 4000 < ν < 5100 cm⁻¹ and 5630 < ν < 7700 cm⁻¹ does induce tautomerization. Narrowband (8 cm⁻¹ fwhm) laser irradiation studies in the NH symmetric plus antisymmetric stretch combination band region (6300 < ν < 6600 cm⁻¹) show that the near infrared-induced tautomerization occurs at select wavelengths. Tautomer conversion in absence of site conversion is strong evidence that the observed photochemistry is due to absorption of light by porphine and not by hexane. The estimated quantum yield is roughly 5×10^{-4} for 6530 cm⁻¹ irradiation; this is one to three orders of magnitude larger than the quantum yield expected from RRKM theory.

4. Work in Progress

Energy-transfer and chemical-reaction rates are being studied for triplet CH₂ radicals. A diode-laser infrared flash kinetic spectrometer is being used to study the reaction with O₂ in order to identify product states and intermediates. Reaction rates of ³CH₂ with O₂ and NO have already been measured, in collaboration with H.S. Johnston. Reaction rates for radical-radical reactions are being measured. Spectroscopy of radical-radical and radical-molecule reaction complexes is planned.

Unimolecular reaction dynamics are being studied by photofragment spectroscopy. The branching between fragmentation on the triplet and singlet surfaces of ketene is being studied by detection of CO fragments

using a tunable photolysis laser below the threshold for singlet fragmentation. The rotational state distribution for CO from dissociation on the singlet surface is much cooler than that for dissociation on the triplet surface.

Infrared spectra of intermediates in organometallic photochemistry in gas and liquid phase are being studied jointly with R.G. Bergman. Emphasis is on CH activation chemistry. Studies of CH activation systems in liquid Kr and Xe are proceeding well.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. D.C. Darwin, A.T. Young, H.S. Johnston, and C.B. Moore, "Rate Constants for ³CH₂($\tilde{X}^3B_1$) Removal by O₂, NO, and C₂H₂ from Infrared Diode Laser Flash Kinetic Spectroscopy," *J. Phys. Chem. Frederick Kaufman memorial issue* **93**, 1074 (1989); LBL-25112.
2. B.H. Weiller, E.P. Wasserman, R.G. Bergman, C.B. Moore, and G.C. Pimentel, "Time-resolved IR Spectroscopy in Liquid Rare Gases: Direct Rate Measurement of an Intermolecular Alkane C-H Oxidative Addition Reaction," *J. Am. Chem. Soc.* **111**, 8288 (1989); LBL-28049.

LBL Reports

3. I-C. Chen and C.B. Moore, "Photofragmentation of Ketene to CH₂($\tilde{X}^3B_1$) + CO: I. Barrier Height And Dissociation Rate Constant," *J. Chem. Phys.* (in press); LBL-26906.
4. I-C. Chen and C.B. Moore, "Photofragmentation of Ketene to CH₂($\tilde{X}^3B_1$) + CO: II. Rotational State Distributions of Product CO," *J. Chem. Phys.* (in press); LBL-26908.
5. T.J. Butenhoff, R.S. Chuck, H.-H. Limbach, and C.B. Moore, "The Near-Infrared Photochemistry of Porphine Imbedded in a n-Hexane Matrix," in *Proc. Int. Conf. Laser Induced Chemistry (FECHIM)*, Bechyne, Czechoslovakia (in press); LBL-28352.
6. T.J. Butenhoff, R.S. Chuck, H.-H. Limbach, and C.B. Moore, "Vibrational Photochemistry of Porphine Imbedded in a n-Hexane-d₁₄ Shpol'skii Matrix," submitted to *J. Phys. Chem.* K.S. Pitzer 75th Birthday issue; LBL-28360.
7. Y. Guo (Ph.D. Thesis), "Spectroscopy and Reaction Kinetics of HCO," LBL-26690.
8. I-C. Chen (Ph.D. Thesis), "Photofragmentation of Ketene to CH₂($\tilde{X}^3B_1$) + CO: Dissociation Rate, Energy Release and Exit Barrier Height," LBL-26906.
9. D.C. Darwin (Ph.D. Thesis), "Chemical Kinetics of Triplet Methylene from Infrared Diode Laser Flash Kinetic Spectroscopy," LBL-28503.
10. E.P. Wasserman, (Ph.D. Thesis), "Reactivity of Coordinatively Unsaturated Organometallic Species in the Gas Phase and in Solution," LBL-28052.

Invited Talks

11. C.B. Moore, "State-Resolved State-Selected Dynamics of Chemical Bond Breaking," acceptance lecture for first Inter-American Photochemical Society Award in Photochemistry, I-APS Conference, Clearwater Beach, FL, Jan. 5, 1989.
12. C.B. Moore, "State-to-State Studies of Unimolecular Reaction Dynamics," XVIIIth Informal Conference on Photochemistry, University of Southern California, Santa Monica, CA, Jan. 12, 1989.
13. C.B. Moore, T.J. Butenhoff, K.L. Carleton, I-C. Chen, Y. Choi, W.H. Green, D.R. Guyer, and W.F. Polik, "The Dynamics of Chemical Bond Breaking in the Quantum State-Resolved Limit," AAAS Annual Meeting, Symposium on Frontiers in Chemistry, San Francisco, CA, Jan. 14-19, 1989.
14. C.B. Moore, "The High Resolution Spectroscopy of Unimolecular Reactions," 1989 Annual Conference, Western Spectroscopy Association, Asilomar, CA, Jan. 26, 1989.
15. C.B. Moore, "State-to-State Studies of the Dynamics of Chemical Bond Breaking," Universidad Complutense, Departamento de Química Física, Madrid, Spain, Feb. 21, 1989.
16. C.B. Moore, "State-to-State Studies of the Dynamics of Chemical Bond Breaking," Universidad Autónoma de Madrid, Facultad de Ciencias, Madrid, Spain, Feb. 22, 1989.
17. C.B. Moore, "State-to-State Studies of the Dynamics of Chemical Bond Breaking," Universidad de Salamanca, Salamanca, Spain, Feb. 23, 1989.
18. C.B. Moore, "High Resolution Spectroscopy of Dissociating Molecules — D_2CO and $HFCO$ " or "Chemical Bond Breaking Dynamics with Complete State Resolution," Laboratoire de Spectrométrie Physique, Université de Grenoble, Saint Martin d'Hères (Grenoble), France, Feb. 27-Mar. 4, 1989.
19. C.B. Moore, "The Dynamics of Chemical Bond Breaking in the State-resolved Limit," Department of Chemistry and Applied Science, Brookhaven National Laboratory, Upton, NY, Mar. 15, 1989.
20. C.B. Moore, Y.S. Choi, D.R. Guyer, W.F. Polik, and Q.-K. Zheng, "Molecular Eigenstate Spectra at the Threshold for Chemical Bond Breaking: Formaldehyde and Formyl Fluoride," Ninth International Conference on Laser Spectroscopy (NICOLS), Bretton Woods, NH, June 18-23, 1989.
21. C.B. Moore, "Lasers and Chemical Principles," Science for Science Teachers Program, Lawrence Hall of Science, Berkeley, CA, June 28, 1989.
22. C.B. Moore, "Lasers in Chemistry," ICE Program in Chemical Instrumentation, Lawrence Hall of Science, Berkeley, CA, June 29, 1989.
23. T.J. Butenhoff, R.S. Chuck, H.-H. Limbach, and C.B. Moore, "The Near-Infrared Photochemistry of Prophine Imbedded in an n-Hexane Matrix," International Conference on Laser Induced Chemistry (FECHEM), Bechnye, Czechoslovakia, Sept. 17, 1989.
24. C.B. Moore, "State-selected Dynamics of Unimolecular Reactions," Allied Engineered Materials, Morristown, NJ, Oct. 4, 1989.
25. C.B. Moore, "Molecular Energy Flow," Combustion Dynamics Workshop, DOE CDRL Review, LBL, Oct. 17, 1989.

Physical Chemistry with Emphasis on Thermodynamic Properties*

Kenneth S. Pitzer, Investigator

INTRODUCTION

The purpose of this program is the discovery and development of methods of calculation of thermodynamic and related properties of important chemical systems by the use of quantum and statistical mechanics together with experimental measurements for key systems. Current emphasis is on novel ionic systems and on properties close to the critical point. Systems comprising fused salts mixed in any proportion with water or other polar solvents are being studied experimentally and with theory. Current studies also include (1) dilute ionic solutions very close to the critical point of the solvent where anomalous properties are observed and (2) the representation of near-critical properties in an equation of state valid over the full range of temperature and density. Recent theoretical advances include treatments of the dielectric constant of H_2O , the thermodynamics of ionic solutions in H_2O above its critical temperature, and the critical properties of pure ionic fluids such as NaCl . Earlier advances yielded improved equations for electrolyte solutions. These various equations are now being applied to a wide variety of systems of industrial or geological interest, including geothermal brines. Other recent research involved the relativistic quantum chemistry of molecules containing very heavy atoms.

1. Thermodynamics of Aqueous Uranyl Sulfate to 559 K (Publication 5)

J.-Z. Yang and K.S. Pitzer

A comprehensive treatment of the thermodynamic properties of aqueous UO_2SO_4 to 559 K is presented. This system has the unusual property of liquid-liquid phase separation above its critical temperature of 559 K. The equations for criticality and for phase equilibria in the molality systems are developed. The factors leading to this

phase separation are discussed, as well as the approximations inherent in our equation because of incomplete information.

2. Relationships in the Approach to Criticality in Fluids, Including Systematic Differences Between Vapor-Liquid and Liquid-Liquid Systems (Publication 2)

R.R. Singh and K.S. Pitzer

The available data on a number of vapor-liquid and liquid-liquid systems have been re-examined. The effective critical exponent β is used to describe the approach to criticality for the two types of systems (see Figure 2-1). The liquid-liquid critical systems have a small or zero first Wegner correction term, and are similar in this respect to the spin 1/2 Ising lattice. The gas-liquid critical systems have a much larger first Wegner term and are qualitatively similar to a high-spin Ising lattice. By analyzing data for a number of fluids, we find strong support for a universal value for the first Wegner coefficient for vapor-liquid coexistence in simple fluids. The higher correction terms are substance dependent. These statements do not apply to ionic fluids, which have quite different properties. The extent to which metals differ or are similar is examined briefly. The substance dependence of the leading critical amplitudes has also been examined with reference to the extensions of the corresponding-states theorem. An approximate linear dependence of the amplitude on the acentric factor of the fluid is found.

Figure 2-1. The effective β for a few accurately measured systems plotted against the reduced temperature. Note the marked difference between the pure fluids (CO_2 and Xe) as compared to the two-component, liquid-liquid systems. The curves for the mean-field models and the Ising ($s = 1/2$) lattice are also shown, together with points for calculated values for the Lennard-Jones potential. (XBL 901-152)

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3. Calculation of the Ionization Constant of H₂O to 2,273 K and 500 MPa (Publication 13)

J.C. Tanger IV and K.S. Pitzer

Calculations of the ionization constant of H₂O are presented for densities ranging from those of subcritical water to those of supercritical steam. A recently proposed semicontinuum model¹ is used to calculate the standard-state hydration properties for the ions, H₃O⁺ and OH⁻. Calculated ionization constants are in good agreement with reported measurements² at pressures from vapor-liquid saturation to 500 MPa and temperatures from 273 to 1,073 K (see Figure 3-1). These measurements cover H₂O densities ranging from ~1,000 to 450 kg • m⁻³. At H₂O densities less than 400 kg • m⁻³, our calculated ionization constants should be more reliable than those obtained from the commonly used equation of Marshall and Franck.³

1. J.C. Tanger IV and K.S. Pitzer, *J. Phys. Chem.* **93**, 4941 (1989) (Publication 11).
2. A.S. Quist, *J. Phys. Chem.* **74**, 3396 (1970).
3. W.L. Marshall and E.U. Franck, *J. Phys. Chem. Ref. Data* **10**, 295 (1981).

Figure 3-1. Calculated values of log K_w vs pressure for H₂O (curves) compared with experimental values of Quist² for two isotherms. (XBL 901-153)

4. Rectilinear Diameters and Extended Corresponding-States Theory (Publication 15)

R.R. Singh and K.S. Pitzer

The amplitude of the rectilinear diameter is examined for a large number of normal fluids and a few other fluids. For the normal fluids, the slope of the diameter shows a linear dependence on the acentric factor, as do other fluid properties on a reduced basis. Thus, we conclude that the shape of the pair potential is the primary factor in determining the slope of the diameter rather than the relative strength of three-body forces, as has been suggested by analogy to recent results for rubidium and cesium. The situation for the near-critical singularity in the diameter remains ambiguous for normal fluids, and a suggestion is made for its resolution.

5. Work in Progress

The liquid-liquid coexistence curve for the newly discovered ionic system (Publication 1) has been extended closer to the critical point at 43.6°C by refractive-index measurements at temperatures controlled to 1 mK. In collaboration with another MCSD group, Monte Carlo simulations are being carried out for two-dimensional fluids as representative of adsorbed monolayers. The Lennard-Jones potential is assumed, and the Gibbs ensemble is adopted for the calculations.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. R.R. Singh and K.S. Pitzer, "An Ionic System with Critical Point at 44°C," *J. Am. Chem. Soc.* **110**, 8723 (1988); LBL-25646.
2. K.S. Pitzer and J.C. Tanger IV, "Near-Critical NaCl-H₂O; An Equation of State and Discussion of Anomalous Properties," *Intl. J. Thermophys.* **9**, 635 (1988); LBL-25630.
3. D.R. Schreiber and K.S. Pitzer, "Selected Equation of State in the Acentric Factor System," *Intl. J. Thermophys.* **9**, 965 (1988); LBL-25452.
4. K.S. Pitzer, "Fluids, Both Ionic and Nonionic, Over Wide Ranges of Temperature and Composition," *J. Chem. Thermodyn.* **21**, 1 (1989); also *Pure & Appl. Chem.* **61**, 979 (1989); LBL-25859.

5. J.-Z. Yang and K.S. Pitzer, "Thermodynamics of Aqueous Uranyl Sulfate to 559 K," *J. Sol. Chem.* **18**, 189 (1989); LBL-25745.
6. J.-Z. Yang and K.S. Pitzer, "The Application of the Ion-Interaction Model to Multicomponent 1-1 Type Electrolytes in Mixed Solvents," *J. Sol. Chem.* **18**, 201 (1989); LBL-26023.
7. K.S. Pitzer, "Some Interesting Properties of Vapor-Liquid or Liquid-Liquid Coexistence Curves for Ionic and Nonionic Fluids," *Thermochim. Acta* **139**, 25 (1989); LBL-25058.
8. J.L. Bischoff and K.S. Pitzer, "Liquid-Vapor Relations for the System NaCl-H₂O: Summary of the P-T-x Surface from 300° to 500°C," *Am. J. Science* **289**, 217 (1989); LBL-25108.[†]
9. R.R. Singh and K.S. Pitzer, "Relationships in the Approach to Criticality in Fluids, Including Systematic Differences Between Vapor-Liquid and Liquid-Liquid Systems," *J. Chem. Phys.* **90**, 5742 (1989); LBL-26534.
10. J.C. Tanger IV and K.S. Pitzer, "Thermodynamics of NaCl-H₂O: a New Equation of State for the Near-Critical Region and Comparisons with Other Equations for Adjoining Regions," *Geochim. et Cosmochim. Acta* **53**, 973 (1989); LBL-24814.
11. J.C. Tanger IV and K.S. Pitzer, "Calculation of the Thermodynamic Properties of Aqueous Electrolytes to 1000°C and 5000 Bar from a Semicontinuum Model for Ion Hydration," *J. Phys. Chem.* **93**, 4941 (1989); LBL-26261.[†]
12. D.R. Schreiber and K.S. Pitzer, "Equation of State in the Acentric Factor System," *Fluid Phase Equilib.* **46**, 113 (1989); LBL-25927.
13. J.C. Tanger IV and K.S. Pitzer, "Calculation of the Ionization Constant of H₂O to 2273 K and 500 MPa," *AIChE J.* **35**, 1631 (1989); LBL-26855.
14. L.M. Connaughton, F.J. Millero, and K.S. Pitzer, "Volume Changes for Mixing the Major Sea Salts: Equations Valid to Ionic Strength 3.0 and Temperature to 95°C," *J. Sol. Chem.* **18**, 1007 (1989); LBL-27304.[†]

LBL Reports

15. R.R. Singh and K.S. Pitzer, "Rectilinear Diameters and Extended Corresponding States Theory," accepted by *J. Chem. Phys.*; LBL-27824.
16. R.R. Singh and K.S. Pitzer, "Near Critical Coexistence Curve and Critical Exponent of an Ionic Fluid," submitted to *J. Chem. Phys.*; LBL-27560.
17. J.K. Hovey, K.S. Pitzer, J.C. Tanger IV, J.L. Bischoff, and R. Rosenbauer, "Vapor-Liquid Phase Equilibria of Potassium Chloride-Water Mixtures; Equation of State Representation for KCl-H₂O and NaCl-H₂O," accepted by *J. Phys. Chem.*; LBL-27558.[†]
18. K.S. Pitzer, "Second Virial Coefficients for Mixed Gases of Low Polarity," submitted to *Fluid Phase Equilib.*; LBL-27989.
19. R.R. Singh, K.S. Pitzer, J.J. de Pablo, and J.M. Prausnitz, "Monte Carlo Simulation of Phase Equilibria for the Two-Dimensional Lennard-Jones Fluid in the Gibbs Ensemble," submitted to *J. Chem. Phys.*; LBL-28069.

Invited Talks

20. K.S. Pitzer, "Equations of State for NaCl-H₂O and Related Systems Above 573 K," 44th Annual Calorimetry Conference, Oak Ridge, TN, July 30-Aug. 4, 1989.
21. J.K. Hovey, K.S. Pitzer, and J.C. Tanger, "Vapor-Liquid Phase Equilibria of Potassium Chloride-Water Mixtures; Equation of State Representation for KCl-H₂O and NaCl-H₂O," 3rd International Symposium on Hydrothermal Reactions, Frunze, U.S.S.R., Sept. 12-15, 1989.[†]
22. K.S. Pitzer, "Ionic Fluids over Wide Ranges of Temperature and Composition," International Chemical Congress of Pacific Basin Societies, Honolulu, HI, Dec. 17-22, 1989.

[†]This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Engineering and Geosciences, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Molecular Interactions*

William A. Lester, Jr., Investigator

INTRODUCTION

This research program is directed at extending fundamental knowledge of atoms and molecules, including their electronic structure, mutual interaction, collision dynamics, and interaction with radiation. The approach combines the use of *ab initio* methods—multiconfiguration Hartree-Fock (MCHF), configuration interaction (CI), and the recently developed quantum Monte Carlo (QMC)—to describe electronic structure, intermolecular interactions, and other properties, with various methods for characterizing inelastic and reactive collision processes, and photodissociation dynamics.

1. Reaction Hamiltonian Method for Chemical Reactions: Effect of Indistinguishable Nuclei (Publication 2)

V.Z. Kresin and W.A. Lester, Jr.

The treatment of chemical reactions based on the theory of quantum transitions developed by the authors has been generalized to include the effects of indistinguishable nuclei. The reaction $\text{HI} + \text{H} \rightarrow \text{H}_2 + \text{I}$, for which population alternation in the H_2 product rotational distributions for $v = 0, 1$, and 2 was recently observed, has been analyzed. The total probability of a quantum-state transition was found to depend on the spin degeneracy factor (as expected) and a nonmonotonic function dependent weakly on j .

2. Nonadiabatic Hamiltonian for Electronic-Vibrational Coupling (Publication 3)

V.Z. Kresin and W.A. Lester, Jr.

A new version of adiabatic theory enabling the evaluation of higher-order nonadiabatic terms to any desired accuracy has been developed. A nonadiabatic Hamiltonian $\hat{H}_{\text{na}}$ is introduced that leads to the total Hamiltonian in the form $\hat{H} = \hat{H}_0 + \hat{H}_{\text{na}}$, where $\hat{H}_0$ describes the noninteracting electronic and nuclear subsystems,

and $\hat{H}_{\text{na}}$ describes the electronic-vibrational coupling. Following the approach the correction to the total energy has been calculated. The theory has been applied to vibrational Raman scattering of aromatic molecules. Nonadiabaticity is found to play a key role in vibrational Raman scattering.

3. Quantum Time-Dependent Study of the Scattering of He by $\text{H}_2(\text{B } 1\Sigma_u^+)$ (Publication 4)

P. Pernot,[†] R.M. Grimes,[‡] W.A. Lester, Jr., and C. Cerjon[§]

A quantum time-dependent treatment of the $\text{He} + \text{H}_2(\text{B } 1\Sigma_u^+)$ encounter provides new insight on the dynamics of the system. Time-resolved product distributions of electronic quenching to the ground state and vibrational energy transfer probabilities for the excited electronic state were obtained for a fixed-collision-angle model. The formation and evolution of an intermediate complex on the excited potential energy surface is found to govern the dynamics of product formation.

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4. Molecular-Cluster Model for Magnetic Iron (Publication 6)

A.C. Pavao,[†] C.A. Taft,[‡] B.L. Hammond, and W.A. Lester, Jr.

Ab initio Hartree-Fock calculations were performed on the quintet spin state of the Fe_2 molecule in order to study the electronic, magnetic, and chemical bonding properties as well as the hyperfine interactions. Good agreement is found with band-theoretical and experimental parameters. The calculations support Pauling's model of occupation and bonding of valence orbitals, resonance of covalent bonds, and conduction-band metallic orbitals. A strong charge-polarization effect is found that is not observed in the septet ground state. The participation of s and d electrons in bonding is similar to that found in recent configuration-interaction calculations on the ground state. The calculated magneton number is in good agreement with experiment.

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5. Work in Progress

Quantum Monte Carlo (QMC) for Molecules

Two QMC algorithms for computing quantum mechanical expectation values of coordinate operators that do not commute with the Hamiltonian were developed and found to yield accuracies and precisions of better than 0.5% in test cases.

Development effort for construction of a full Green's function QMC computer code have begun. In addition, initial steps towards implementing a method to "release" nodes have been taken.

Transition-Metal Ions and Complexes

In the quest to extend understanding of transition-metal chemistry, a very difficult area of quantum chemistry, and in preparation for damped-core QMC studies of these and similar systems, ground and excited states of Fe_2 and FeS_2^{n-} ($n = 8, 9, 10$) are being studied.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. Z. Sun, P.J. Reynolds, R.K. Owen, and W.A. Lester, Jr., "Monte Carlo Study of Electron Correlation Functions for Small Molecules," *Theor. Chim. Acta* **75**, 353 (1989); LBL-24095.
2. V.Z. Kresin and W.A. Lester, Jr., "Reaction Hamiltonian Method for Chemical Reactions: Effect of Indistinguishable Nuclei," *Chem. Phys. Lett.* **159**, 297 (1989); LBL-27335.
3. V.Z. Kresin and W.A. Lester, Jr., "Nonadiabatic Hamiltonian for Electronic-Vibrational Coupling," *Int. J. Quant. Chem. Quantum Chem. Symp.* **23**, 17 (1989); LBL-26867.
4. P. Pernot, R.M. Grimes, W.A. Lester, Jr., and C. Cerjan, "Quantum Time-Dependent Study of the Scattering of He by $\text{H}_2(\text{B } ^1\Sigma_u^+)$," *Chem. Phys. Lett.* **163**, 297 (1989); LBL-27770.
5. M. Braga, S.K. Lie, C.A. Taft, and W.A. Lester, Jr., "Electronic Structure, Hyperfine Interactions and Magnetic Properties for Iron Octahedral Sulfides," *Phys. Rev. B* **38**, 10837 (1988); LBL-25939.
6. A.C. Pavao, C.A. Taft, B.L. Hammond, and W.A. Lester, Jr., "Molecular Cluster Model for Magnetic Iron," *Phys. Rev. B* **40**, 2879 (1989); LBL-28453.
7. B.L. Hammond, M. Braga, C.A. Taft, and W.A. Lester, Jr., "Theoretical Study of the Interaction of Ionized Transition Metals (Cr, Mn, Fe, Co, Ni, Cu) with Argon," accepted by *Phys. Rev. B*; LBL-28454.
8. B. Kim, B.L. Hammond, W.A. Lester, Jr., and H.S. Johnston, "Ab Initio Study of the Vibrational Spectra of NO_3 ," accepted by *Chem. Phys. Lett.*; LBL-28434.
9. P. Pernot and W.A. Lester, Jr., "Multidimensional Wave-Packet Analysis: Splitting Method for Time-Resolved Property," submitted to *J. Chem. Phys.*; LBL-28455.
10. V.Z. Kresin and W.A. Lester, Jr., "Method of Non-Adiabatic Hamiltonian in the Theory of Electron-Vibrational Coupling: Application to Raman Scattering and Phosphorescence," *Bull. Am. Phys. Soc.* **34**, 499 (1989); LBL-26887.
11. W.A. Lester, Jr., and B.L. Hammond, "Quantum Monte Carlo for the Electronic Structure of Atoms and Molecules," accepted by *Ann. Rev. Phys. Chem.*; LBL-28715.
12. B.L. Hammond (Ph.D. Thesis), "Monte Carlo for the Electronic Structure of Molecules," LBL-26536.
13. S.-Y. Huang (Ph.D. Thesis), "The Reaction of Oxygen with Allene," LBL-26537.
14. W.A. Lester, Jr., AAAS Workshop on "Graduate Studies in Science and Engineering: Games Your Advisor Should Have Taught You," San Francisco, CA, Jan. 17, 1989.
15. W.A. Lester, Jr., "Quantum Study of the Scattering of $\text{H}_2(\text{B } ^1\Sigma_u^+, v, j)$ by He," 16th Annual Meeting, National Organization of Black Chemists and Chemical Engineers, Chicago, IL, Mar. 21-24, 1989.
16. W.A. Lester, Jr., "Nonadiabatic Hamiltonian for Electronic-Vibrational Coupling," and "Quantum Molecular Dynamics and Reactive Scattering," 1989 Sanibel Symposia, St. Augustine, FL, Apr. 2-8, 1989.
17. W.A. Lester, Jr., "Quantum Monte Carlo from the Perspective of a Quantum Chemist," and "Effective-Core Methods in QMC," CECAM Workshop on Quantum Monte Carlo for Molecular Systems, Paris, France, May 14-27, 1989.
18. W.A. Lester, Jr., "Theoretical Studies of Molecular Interactions," Combustion Research Conference, Long Island, NY, June 7-9, 1989.

LBL Reports

Invited Talks

Spectroscopy and Structures of Reactive Intermediates*

Richard J. Saykally, Investigator

INTRODUCTION

The objective of this research is to develop new techniques for the detection of unstable forms of molecules, and to use these techniques to carry out detailed measurements of the structures, properties, and dynamics of these species with the goal of improving our large-scale understanding of chemical reactions and energy transfer, as applied to combustion systems.

Reactive forms of molecules, including neutral-free radicals and molecular ions, play extremely important roles as reaction intermediates in combustion processes, reactive plasmas, in the terrestrial atmosphere, and in interstellar space. The transient nature of these reactive species has made their detection and characterization a very difficult task, and comparatively few of these important reactive molecules have been studied in detail.

"van der Waals complexes"—molecules held together at low temperatures only by very weak dispersion or induction forces or by hydrogen bonds—constitute excellent prototypes of these same weak interactions that dominate the condensed phases. One of the chemical physicist's great dreams has been to bridge the gap from the gas phase, where detailed measurements of isolated species are possible, to the condensed phase, where this is clearly impossible, through the investigation of successively more complex van der Waals aggregates in the gas phase. This dream is still a long way from being realized, as these species, like the reaction intermediates, are extremely difficult to detect and characterize. Nevertheless, a new level of understanding of van der Waals forces is emerging from studies of the vibrational motions of the weak bonds.

The primary goal of this research, then, is to carry out detailed investigations of those reaction intermediates that are critical species in the combustion of important fuels. Exactly the same experimental and theoretical techniques employed to study reaction intermediates can be applied to van der Waals molecules; hence, studies of these two crucially important classes of molecules will be undertaken

as well, with the long-range objective of correlating the measured properties of these species as a means of understanding condensed phases in more detail.

1. Measurement of the Perpendicular Rotation-Tunneling Spectrum of the Water Dimer by Tunable Far-Infrared Laser Spectroscopy in a Planar Supersonic Jet (Publication 6)

K.L. Busarow, R.C. Cohen, G.A. Blake,[†] K.B. Laughlin,[‡] Y.T. Lee, and R.J. Saykally

Fifty-six transitions from the $K = 1$ lower $\rightarrow K = 2$ tunneling-rotation band of water dimer have been measured and assigned at 22 cm^{-1} by direct absorption spectroscopy in a continuous-wave planar supersonic jet expansion using a tunable far-infrared laser spectrometer. Two different models were used to fit the data, and several spectroscopic constants were determined for the upper and lower states. This work supports the local IAM model recently proposed by Coudert and Hougen for the hydrogen bond tunneling motions, all of which contribute to the observed tunneling splittings. This is the most complicated hydrogen bonded system considered to be well understood at this time, at least in the lowest few K -states.

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2. Far-Infrared Laser Spectroscopy of van der Waals Bonds: A Powerful New Probe of Intermolecular Forces (Publication 9)

R.J. Saykally

A new approach to the determination of intermolecular potential surfaces is described. Far-infrared laser experiments are used to precisely measure intermolecular vibration-rotation-tunneling transitions in weakly bound complexes generated and cooled in supersonic jets. Because the intermolecular vibrational motions possess very large amplitude, they sample large regions of the potential surface. Modern numerical techniques are used to invert the spectra, producing intermolecular potential surfaces that exhibit a level of detail and precision not before accessible even with the most advanced molecular-beam scattering methods.

*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

3. Tunable Far-Infrared Laser Spectroscopy of Ultracold Free Radicals (Publication 12)

R.C. Cohen, K.L. Busarow, C.A. Schmuttenmaer, Y.T. Lee, and R.J. Saykally

We report a new high-resolution spectroscopic technique designed for the study of short-lived free radicals and clusters containing free radicals. Excimer-laser photolysis of a suitable precursor during the initial stages of a planar supersonic expansion is used to generate ultracold free radicals that are subsequently probed by a tunable far-infrared laser. A detection limit of 10^8 molecules/cm³ for light hydrides is demonstrated, and prospects for two to three orders of magnitude improvement are discussed.

4. Work in Progress

We are now developing tunable far-infrared laser techniques for studying complexes of reactive molecules generated by excimer laser photolysis and van der Waals complexes. Ultimately these will possess extremely high sensitivity and resolution so that subtle effects such as hydrogen tunneling migration effects can be explored in fluxional radicals like vinylidene and vinyl radical.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. K.B. Laughlin, G.A. Blake, R.C. Cohen, and R.J. Saykally, "Experimental Determination of Dipole Moments for Molecular Ions: Improved Measurements for ArH⁺," *J. Chem. Phys.* **90**, 1358 (1989).
2. N.H. Rosenbaum, J.C. Owrtusky, and R.J. Saykally, "Velocity Modulation Infrared Laser Spectroscopy of HCS⁺: Analysis of Hot Bands and Perturbations," *J. Mol. Spectrosc.* **133**, 365 (1989).
3. K.G. Lubic, D. Ray, D.C. Hovde, L. Veseth, and R.J. Saykally, "Laser Magnetic Resonance Rotational Spectroscopy of the Hydrogen Halide Molecular Ions: H³⁵Cl⁺ and H³⁷Cl⁺," *J. Mol. Spectrosc.* **134**, 1 (1989).
4. K.G. Lubic, D. Ray, D.C. Hovde, L. Veseth, and R.J. Saykally, "Laser Magnetic Resonance Rotational Spectroscopy of the Hydrogen Halide Molecular Ions: H⁷⁹Br⁺ and H⁸¹Br⁺," *J. Mol. Spectrosc.* **134**, 21 (1989).
5. J.V. Coe, J.C. Owrtusky, E.R. Keim, N.V. Agman, D.C. Hovde, and R.J. Saykally, "Sub-Doppler Direct IR Laser Absorption Spectroscopy in Fast Ion Beams: The Fluorine Hyperfine Structure of HF⁺," *J. Chem. Phys.* **90**, 3893 (1989).
6. K.L. Busarow, R.C. Cohen, G.A. Blake, K.B. Laughlin, Y.T. Lee, and R.J. Saykally, "Measurement of the

Perpendicular Rotation-Tunneling Spectrum of the Water Dimer by Tunable Far Infrared Laser Spectroscopy in a Planar Supersonic Jet," *J. Chem. Phys.* **90**, 3937 (1989); LBL-26174.

7. M. Polak, M.H.W. Gruebele, B.W. DeKock, and R.J. Saykally, "Velocity Modulation Infrared Laser Spectroscopy of Molecular Ions: The ν_4 Band of Ammonium," *Mol. Phys.* **66**, 1193 (1989).
8. J.R. Heath, A.L. Cooksy, M.H.W. Gruebele, C.A. Schmuttenmaer, and R.J. Saykally, "Diode Laser Absorption Spectroscopy of Supersonic Carbon Cluster Beams: The ν_3 Spectrum of C₅," *Science* **244**, 564 (1989).
9. R.J. Saykally, "Far-Infrared Laser Spectroscopy of van der Waals Bonds: A New Probe of Intermolecular Forces," *Acc. Chem. Res.* **22**, 295 (1989); LBL-26553.
10. J.C. Owrtusky, E.R. Keim, J.V. Coe, and R.J. Saykally, "Absolute IR Intensities of the ν_3 Bands of HN₂⁺ and HCO⁺ Determined by Direct Laser Absorption Spectroscopy in Fast Ion Beams," *J. Phys. Chem.* **93**, 5960 (1989).
11. D.C. Hovde, E.R. Keim, and R.J. Saykally, "Velocity Modulation Laser Spectroscopy of Molecular Ions: The Hyperfine-Resolved Rovibrational Spectrum of HF⁺," *Mol. Phys.* **68**, 599 (1989).
12. R.C. Cohen, K.L. Busarow, C.A. Schmuttenmaer, Y.T. Lee, and R.J. Saykally, "Tunable Far Infrared Laser Spectroscopy of Ultracold Free Radicals," *Chem. Phys. Lett.* **164**, 321 (1989); LBL-27939.
13. R.C. Cohen, K.L. Busarow, Y.T. Lee, and R.J. Saykally, "Tunable Far Infrared Laser Spectroscopy of van der Waals Bonds: The Intermolecular Stretching Vibration and Effective Radial Potentials for Ar-H₂O," *J. Chem. Phys.* **92**, 169 (1990); LBL-27537.

LBL Reports

14. M. Havenith, D.-H. Gwo, K. Busarow, R.C. Cohen, and R.J. Saykally, "Measurement of the Intermolecular Vibration-Rotation-Tunneling Spectrum of Ammonia Dimer by Tunable Far Infrared Laser Spectroscopy in a Planar Supersonic Jet," submitted to *J. Chem. Phys.*; LBL-28446.
15. D.-H. Gwo, M. Havenith, R.C. Cohen, K. Busarow, and R.J. Saykally, "Tunable Far-IR Laser Spectroscopy of van der Waals Bonds: The Intermolecular Stretching Vibration of Ar-NH₃," submitted to *J. Chem. Phys.*; LBL-28447.
16. R.J. Saykally, "Tunable Far-Infrared Laser Spectroscopy" (invited review article), submitted to *Rev. Sci. Instrum.*; LBL-28448.

Invited Talks

17. R.J. Saykally, "Spectroscopy of Molecular Ions: Direct Laser Absorption Spectroscopy in Fast Ion Beams (DLASIB)," Bomem Michelson Prize Lecture, Pittsburgh Conference, Atlanta, GA, Mar. 9, 1989.
18. R.J. Saykally, "Infrared Spectroscopy of Molecular Ions and Carbon Clusters," Department of Chemistry, Emory University, Atlanta, GA, Mar. 10, 1989.

19. R.J. Saykally, "Spectroscopy of Molecular Ions: Direct Laser Absorption Spectroscopy in Fast Ion Beams (DLASFIB)," E.K. Plyler Prize Lecture, American Physical Society Meeting, St. Louis, MO, Mar. 21, 1989.
20. R.J. Saykally, "Ions and Clusters: Some New Experiments," Department of Chemistry, University of Colorado, Boulder, Apr. 28, 1989.
21. R.J. Saykally, "Spectroscopy of Molecular Ions: Direct Laser Absorption Spectroscopy in Fast Ion Beams (DLASFIB)," American Society for Mass Spectrometry, Miami Beach, FL, May 23, 1989.
22. R.J. Saykally, "IR Laser Spectroscopy of Supersonic Carbon Clusters," ILS Conference, Stanford, CA, Aug. 28, 1989.
23. R.J. Saykally, "Tunable Far-IR Laser Spectroscopy of Weakly Bound Clusters," American Chemical Society National Meeting, Miami, FL, Sept. 1989.
24. R.J. Saykally, "IR Laser Spectroscopy of Supersonic Carbon Clusters," American Chemical Society National Meeting, Miami, FL, Sept. 1989.
25. R.J. Saykally, "Infrared Laser Spectroscopy of Supersonic Carbon Clusters," Naval Research Laboratory, Washington, DC, Oct. 19, 1989.
26. R.J. Saykally, "Tunable Far-IR Laser Spectroscopy of Clusters: A New Probe of Intermolecular Forces and Intramolecular Dynamics," Chemistry Colloquium, University of Illinois at Urbana-Champaign, Urbana, IL, Nov. 2, 1989.

Theory of Atomic and Molecular Collision Processes*

William H. Miller, Investigator

INTRODUCTION

This research is primarily involved with the development and application of theoretical methods and models for describing atomic and molecular collision processes and chemical reaction dynamics. Specific topics of interest have included the theory of inelastic and reactive scattering, collision processes involving electronically excited atoms or molecules, collisional ionization phenomena, statistical theories of chemical reactions, scattering of atoms and molecules from surfaces, and the interactions of molecular systems with high-power laser radiation.

Most recently, research has focused on the development of theoretical methods for a first-principles treatment of dynamics in polyatomic molecular systems. The goal is to develop approaches that can utilize *ab initio* quantum chemical calculations of the potential energy surface (in the Born-Oppenheimer approximation) as direct input into the dynamical treatment, and thus, to as great an extent as possible, have a truly predictive theory.

The potential application of these methods is almost without limit. In this group hydrogen-atom transfer processes have been studied in a variety of systems. Other research groups have used these approaches to describe a variety of reactions that are relevant to the primary steps in combustion.

1. A Semiclassical Tunneling Model for Use on Classical Trajectory Simulations (Publication 5)[†]

N. Makri[‡] and W.H. Miller

A semiclassical model for tunneling from one classically allowed region on a potential energy surface to another is described. The principal feature on this model, compared to earlier (more "rigorous") multidimensional semiclassical tunneling theories, is that it can be implemented in a straightforward way within the framework of a standard classical trajectory simulation. Applications to several examples of unimolecular

isomerization and unimolecular dissociation show that the model is capable of providing excellent results over a wide range of conditions (i.e., coupling strengths, different symmetries of couplings, etc.).

[†]Calculations were performed on the Berkeley Theoretical Chemistry computing facility, supported in part by National Science Foundation Grant No. CHE84-16345.

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2. Quantum Reactive Scattering via the S-Matrix Version of the Kohn Variational Principle: Differential and Integral Cross Sections for $D + H_2 \rightarrow HD + H$ (Publication 3)[†]

J.Z.H. Zhang and W.H. Miller

A comprehensive survey of the quantum-scattering methodology that results from applying the S-matrix version of the Kohn variational principle to the reactive-scattering formulation given by Miller¹ is presented. Results of calculations using this approach are reported for the reaction $D + H_2 \rightarrow HD + H$. The 3D calculations include total angular momentum values from $J = 0$ up to 31 in order to obtain converged integral and differential cross sections over a wide range of energy (0.4–1.35 eV total energy). Results are given for reaction probabilities for individual values of J , integral and differential cross sections for a number of energies, and state-to-state rate constants (i.e., a Boltzmann average over translational energy), and comparisons are made to a variety of different experimental results. A particularly interesting qualitative feature observed in the calculations is that the energy dependence of the differential cross section in the backward direction ($\theta = 180^\circ$) shows a resonance structure (due to a short-lived DH_2 collision complex) that is very similar to that in the $J = 0$ reaction probability. This resonance structure does not appear in the energy dependence of the integral cross section, being averaged out by the sum over J .

Figure 2-1 shows the reaction probability for $D + H_2$ ($v = j = 0 \rightarrow HD(v', \text{all } j') + H$), as a function of energy, for total angular momentum $J = 0$. Resonance structures due to short-lived collision complexes are clearly visible. Figure 2-2, however, shows that in the physically observable cross section for this reaction—which involves a sum of J values from 0 to ~ 30 —these features are averaged out (cf. inhomogeneous broadening).

[†]Calculations were performed on the CRAY 2 supercomputer at the NASA-Ames Research Center, supported by National Science Foundation Grant No. CHE84-16345.

1. W. Miller, J. Chem. Phys. **50**, 407 (1969).

*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Figure 2-1. Reaction probability for $D + H_2 (v = j = 0) \rightarrow HD (v', \text{all } j') + H$ for $J = 0$, as a function of total energy. (XBL 902-496)

3. On the Absence of Anomalous Singularities in the S-Matrix Version of the Kohn Variational Principle for Quantum Scattering (Publication 6)[†]

L.F.X. Gaucher and W.H. Miller

Recent calculations by Apagyi, Lévy, and Ladányi¹ have shown that anomalous (i.e., spurious, unphysical) singularities arise in $e^- + H(1s)$ scattering calculations using the Schwinger variational principle. It has long been known that such singularities can exist in the K-matrix version of the Kohn variational principle, but this is the first time (to our knowledge) that they have been seen in the Schwinger variational principle. This paper reports the results of calculations for this same problem using the S-

Figure 2-2. (Converged) integral cross sections for $D + H_2 (v = j = 0) \rightarrow HD (v', \text{all } j')$, as a function of energy. (XBL 902-497)

matrix version of the Kohn variational principle,² showing that there are no such anomalous singularities in this approach.

[†]Calculations were performed on the Berkeley Theoretical Chemistry computing facility, supported in part by National Science Foundation Grant No. CHE84-16345.

1. B. Apagyi, P. Lévy, and K. Ladányi, *Phys. Rev. A* **37**, 4577 (1985).
2. J.Z.H. Zhang, S.I. Chu, and W.H. Miller, *J. Chem. Phys.* **88**, 6233 (1988).

4. A Simple Model for Correcting the Zero-Point Energy Problem in Classical Trajectory Simulations of Polyatomic Molecules (Publication 8)[†]

W.H. Miller, W.L. Hase,[‡] and C.L. Darling

A simple model is proposed for correcting problems with zero-point energy in classical trajectory simulations of dynamical processes in polyatomic molecules. The "problems" referred to are that classical mechanics allows the vibrational energy in a mode to decrease below its quantum zero-point value, and since the total energy is conserved classically this can allow too much energy to pool on other modes. The proposed model introduces hard-sphere-like terms in action-angle variables that prevent the vibrational energy in any mode from falling below its zero-point value. The algorithm that results is quite simple in terms of the Cartesian normal modes of the system: if the energy in a mode k , say, decreases below its zero-point value at time t , then at this time the momentum P_k for that mode has its sign changed, and the trajectory continues. This is essentially a time reversal for mode k (only!), and it conserves the total energy of the system. One can think of the model as supplying impulsive "quantum kicks" to a mode whose energy attempts to fall below its zero-point value, a kind of "Planck demon" analogous to a Brownian-like random force. The model is illustrated by application to a model of CH overtone relaxation.

[†]Calculations were performed on the Berkeley Theoretical Chemistry computing facility, supported in part by National Science Foundation Grant No. CHE84-16345.

[‡]Permanent address: Department of Chemistry, Wayne State University, Detroit, MI 48202.

5. Work in Progress

One of the most difficult steps in theoretical modeling of dynamical processes in polyatomic molecules is construction of the potential energy surface. Reaction-path models are very useful because they require only local knowledge of the potential, but there are times when a global potential function is necessary. Ideas are being

developed for using an empirical valence-bond model that will make this possible.

Also, further developments of the S-matrix Kohn scattering methodology should make it possible to study reactions such as $\text{H} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{OH}$ at this rigorous level of theory.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. N. Makri and W.H. Miller, "Exponential Power Series Expansion for the Quantum Time Evolution Operator," *J. Chem. Phys.* **90**, 904 (1989); LBL-26701.
2. J.Z.H. Zhang and W.H. Miller, "Reply to Comment on: Accurate Three-Dimensional Quantum Scattering Calculations for $\text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H}$," *J. Chem. Phys.* **90**, 7610 (1989).
3. J.Z.H. Zhang and W.H. Miller, "Quantum Reactive Scattering via the S-Matrix Version of the Kohn Variational Principle: Differential and Integral Cross Sections for $\text{D} + \text{H}_2 \rightarrow \text{HD} + \text{H}$," *J. Chem. Phys.* **91**, 1528 (1989); LBL-26853.
4. J.Z.H. Zhang and W.H. Miller, "Differential Cross Section (Angular Distribution) for the Reaction $\text{H} + \text{H}_2 (\nu = j = 0) \rightarrow \text{H}_2 (\nu', \text{odd } j') + \text{H}$ in the Energy Range 0.90–1.35 eV," *Chem. Phys. Lett.* **159**, 130 (1989).
5. N. Makri and W.H. Miller, "A Semiclassical Tunneling Model for Use in Classical Trajectory Simulations," *J. Chem. Phys.* **91**, 4026 (1989); LBL-26721.
6. L.F.X. Gaucher and W.H. Miller, "On the Absence of Anomalous Singularities in the S-Matrix Version of the Kohn Variational Principle of Quantum Scattering," *Isr. J. Chem.* **29**, 349 (1989); LBL-26854.
7. G.A. Voth, D. Chandler, and W.H. Miller, "Time Correlation Function and Path Integral Analysis of Quantum Constants," *J. Phys. Chem.* **93**, 7009 (1989).
8. W.H. Miller, W.L. Hase, and C.L. Darling, "A Simple Model for Correcting the Zero Point Energy Problem in Classical Trajectory Simulations of Polyatomic Molecules," *J. Chem. Phys.* **91**, 2863 (1989); LBL-27281.
9. W. Yang and W.H. Miller, "Block Lanczos Approach Combined with Matrix Continued Fraction for the S-Matrix Kohn Variational Principle in Quantum Scattering," *J. Chem. Phys.* **91**, 3504 (1989).
10. W. Yang, A.C. Peet, and W.H. Miller, "Collocation Approach for Quantum Scattering Based on the X-Matrix Kohn Variational Principle," *J. Chem. Phys.* **91**, 7537 (1989).
11. G.A. Voth, D. Chandler, and W.H. Miller, "Rigorous Formulation of Quantum Transition State Theory and its Dynamical Corrections," *J. Chem. Phys.* **91**, 7749 (1989).
12. N. Makri, "Effective Non-Oscillatory Propagator for Feynman Path Integration on Real Time," *Chem. Phys. Lett.* **159**, 489 (1989); LBL-27280.

Other Publications

13. W.H. Miller, "Theoretical Models for Reaction Dynamics in Polyatomic Molecular Systems," in *New Theoretical Concepts for Understanding Organic Reactions*, J. Bertran and I.G. Csizmadia, Eds., NATO ASI Series, Vol. 267, 1989, p. 347; LBL-25671.
14. W.H. Miller, "Quantum Mechanics of Chemical Reactions: Recent Developments in Reactive Scattering and in Reaction Path Hamiltonians," in *Perspectives in Quantum Chemistry*, B. Pullman and J. Jortner, Eds., (6th Int. Cong. Quant. Chem., Jerusalem), D. Reidel, 1989, p. 57; LBL-26377.
15. W.H. Miller, Y.T. Chang, and N. Makri, "Some New Theoretical Methods for Treating Reaction Dynamics in Polyatomic Molecular Systems," NATO ASI, Turkey, 1989; LBL-27940.
16. G.A. Voth, D. Chandler, and W.H. Miller, "A New Perspective on Quantum Mechanical Transition State Theory," in *Proc. "Quantum Simulations of Condensed Matter Phenomena"*, World Scientific Press, Teaneck, NJ, 1990, p. 391; LBL-28355.

LBL Reports

17. J.Z.H. Zhang and W.H. Miller, "Photodissociation and Continuum Resonance Raman Cross Sections, and General Franck-Condon Intensities, from S-Matrix Kohn Scattering Calculations, with Application to the Photoelectron Spectrum of $\text{H}_2\text{F}^+ + \text{H}\nu \rightarrow \text{H}_2\text{F}, \text{HF} + \text{H} + \text{e}^-$," submitted to *J. Chem. Phys.*; LBL-27936.

Invited Talks

18. W.H. Miller, "Quantum Mechanical Reactive Scattering: Nature's Most Precise Description of a Chemical Reaction," Otto M. Smith Lecture, Oklahoma State University, Stillwater, Mar. 30, 1989.
19. W.H. Miller, "Quantum Reactive Scattering via the S-Matrix Version of the Kohn Variational Principle," Sanibel Symposium on Atomic, Molecular, and Condensed Matter, St. Augustine, FL, Apr. 1–8, 1989.
20. W.H. Miller, "Diabatic Reaction Path Hamiltonian," Symposium on Relaxation and Dynamics in Complex Media, American Chemical Society National Meeting, Dallas, TX, Apr. 9–14, 1989.
21. W.H. Miller, "Topics in Semiclassical Scattering Theory," Conference on Chaos and Quantum Mechanics, Institute for Theoretical Physics, Santa Barbara, CA, June 26–29, 1989.
22. W.H. Miller, "Recent Development in the Theory and Application of Quantum Scattering Theory for Chemical Reactions," International Conference on the Physics of Electronic and Atomic Collisions, New York, NY, July 26–Aug. 1, 1989.
23. W.H. Miller, "Reaction Dynamics of Polyatomic Molecular Systems," NATO Advanced Study Institute on Computational Advances in Organic Chemistry, Altinolu, Turkey, July 30–Aug. 12, 1989.

24. W.H. Miller, "Semiclassical and Quantum Mechanical Rate Constants for Chemical Reactions," Workshop on Quantum Simulations of Condensed Matter Phenomena, Center for Non-Linear Studies, Los Alamos, NM, Aug. 8-11, 1989.
25. W.H. Miller, "Recent Developments in the Theory of Quantum Mechanical Reactive Scattering and its Applications to Simple Chemical Reactions," 3rd International Symposium on Elementary Processes and Chemical Reactivity, Liblice, Czechoslovakia, Sept. 4-8, 1989.
26. W.H. Miller, "Recent Developments in the Theory of Quantum Mechanical Reactive Scattering and its Application to Simple Chemical Reactions," Adriatico Research Conference on Computation in Physics and Physics in Computation, International Centre for Theoretical Physics, Trieste, Italy, Sept. 5-8, 1989.
27. W.H. Miller, "Photodissociation and Continuum Resonance Raman Cross Sections from S-Matrix Kohn Scattering Calculations; Photoelectron Spectrum of $F-H_2 + h\nu \rightarrow F + H_2, HF + H + e^-$," Symposium on Novel Methods for Probing the Transition State (National ACS Meeting), Miami Beach, FL, Sept. 10-15, 1989.
28. W.H. Miller, "Hydrogen Atom Transfer Reactions in Polyatomic Molecules—Classical and Quantum Approaches," Symposium on Chemical Rate Processes in Condensed Phases: 100 Years After Arrhenius (National ACS Meeting), Miami Beach, FL, Sept. 10-15, 1989.

Chemical Physics at High Photon Energies*

David A. Shirley, Investigator

INTRODUCTION

This program addresses both experimental and theoretical aspects of electron spectroscopy for the investigation of electronic structure of matter in the gaseous and condensed phases. Research is conducted using both laboratory sources at LBL and synchrotron radiation in the 5–5000 eV energy range available at SSRL, NSLS, and BESSY, with emphasis on developing the spectroscopy of this newly accessible range of the electromagnetic spectrum. Time-of-flight measurements with synchrotron radiation are used to measure angular distributions of photoelectrons and resonant photoemission phenomena in the gas phase. Of special interest are ultrahigh-resolution absorption and threshold photoemission studies. Ultrahigh-resolution photoelectron spectroscopy based on molecular beams is yielding new information about small molecules and about the transition from single metal atoms to behavior characteristic of a three-dimensional solid. Employing angle-resolved, variable-energy photoemission, this program examines the electronic structure of solids. The program also studies the geometric and electronic structure of surface-adsorbate systems using photoelectron diffraction and angle-resolved photoemission extended fine structure (ARPEFS).

1. Threshold Photoelectron Spectrum of the Argon 3s Satellites (Publication 5)

L.J. Medhurst, A. Schach von Wittenau, R.D. van Zee, J.S. Zhang, S.H. Liu, D.A. Shirley, and D.W. Lindle[†]

Lately a variety of techniques have been used to study the electron correlation satellites with binding energies between the Argon 3s binding energy (29.24 eV) and the 2p⁻² ionization potential (43.38 eV). One of these techniques, threshold photoelectron spectroscopy, with ~90 meV FWHM resolution, revealed at least 25 individual electronic states. All of these could contribute to any other

*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. It was performed at the Stanford Synchrotron Radiation Laboratory, which is supported by the Department of Energy's Office of Basic Energy Sciences.

satellite spectrum, and this fact helped explain some discrepancies between previous measurements. This technique has been applied to the same region with higher resolution (<60 meV at the Ar 3s⁻¹ peak). In this higher-resolution spectrum, at least 29 individual electronic states are present. In some cases the multiplet splitting is observed (see Figure 1-1).

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2. Vibrational Spectra of Se₂⁺ and Te₂⁺ in Their Ground States (Publication 4)

L.-S. Wang, B. Niu, Y.T. Lee, and D.A. Shirley

Vibrationally resolved photoelectron spectra of Se₂⁺ and Te₂⁺ in their ground states were measured using a newly constructed high-temperature supersonic molecular beam source. Ionization potential and fundamental spectroscopic constants for the molecular ions were obtained (see Figure 2-1).

3. High-Temperature and High-Resolution UV Photoelectron Spectroscopy Using Supersonic Molecular Beams (Publication 6)

L.-S. Wang, J.E. Reutt-Robey,[†] B. Niu, Y.T. Lee, and D.A. Shirley

A high-temperature molecular beam source with electron-bombardment heating has been built for high-resolution photoelectron spectroscopic studies of high-

Figure 1-1. Zero-kinetic-energy spectrum of argon from the 3s threshold to the double-ionization limit. Data points are uncorrected for second-order light. The smooth line is a least-squares fit to the data. (XBL 906-2051)

Figure 2-1. The HeI (584 Å) photoelectron spectrum of Se_2^+ , $2\Pi_{g1/2}$, and $2\Pi_{g3/2}$ states, taken at 720 K. HB is a hot band. (XBL 906-2052)

temperature species and clusters. This source has the advantages of: (1) producing an intense, continuous, seeded molecular beam, and (2) eliminating the interference of the heating mechanism from the photoelectron measurement. Coupling the source with our hemispherical electron energy analyzer, we can obtain very high resolution HeI α (584 Å) photoelectron spectra of high-temperature species. Vibrationally resolved photoelectron

spectra of PbSe , As_2 , As_4 , and ZnCl_2 are shown to demonstrate the performance of the new source (see Figure 3-1).

†Permanent address: Department of Chemistry, University of Maryland, College Park, MD 20742.

4. High-Resolution Results from the LBL 55-Meter SGM at SSRL Near the K-Edge of Carbon and Nitrogen (Publication 11)

P.A. Heimann, F. Senf,[†] W. McKinney,[‡] M. Howells,[‡] R.D. van Zee, L.J. Medhurst, T. Lauritzen,[‡] J. Chin,[‡] J. Meneghetti,[‡] W. Gath,[‡] H. Hogrefe,[‡] and D.A. Shirley

The performance of a 55-meter spherical grating monochromator (SGM) is described. A resolution of 60 meV has been achieved at 400 eV, inferred from the linewidths of the nitrogen $1s-\pi^*$ resonance (see Figure 4-1). A photon flux of 4×10^{10} photons/sec has been observed at 440 eV (and with 0.5 eV resolution). An initial experiment has studied the core-shell resonances of gas-phase ethylene, C_2H_4 . Vibrational fine structure was resolved both for the carbon $1s-\pi^*$ and carbon $1s$ -Rydberg excitations. Comparison with the vibrational frequencies of ground-state ethylene implies that the ν_1 (C-H stretch) and ν_2 (C-C stretch) or ν_3 (H-C-H bend) are excited. It is suggested that

Figure 3-1. A schematic view of the high-temperature molecular beam source: (1) rods for fine alignment of the nozzle and skimmer (one of three shown), (2) ceramic spacer, (3) guiding rod, spring, and lock nuts for spring loading (one of three shown), (4) clamp base plate (receiving spring force), (5) water cooling block, (6) water-cooled thermal shield, (7) oven assembly, (8) reducer cap, (9) water cooling coil, (10) triple-tubed flange, (11) carrier gas inlet line, (12) ceramic insulating tube, (13) emission return conductor, (14) stainless steel arm, (15) bellows, (16) XYZ translation stage, (17) filament busbar, (18) vacuum feedthrough. Not shown are the various water lines and thermocouples. All water lines have electrical breaks and are made of flexible tubing or plastic tubing to free the motion of the stainless steel arm. (XBL 8712-10502)

Figure 4-1. The $1s-\pi^*$ photoabsorption resonance of nitrogen gas accumulated with $10\text{-}\mu$ slit openings. The points represent the experimental data, while the solid line shows a fit with five Voigt functions (Lorentzian width: 128 meV, Gaussian width: 80 meV). (XBL 906-2053)

the lower Rydberg orbitals, $3s$ and $3p\sigma$, have molecular, antibonding character.

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[‡]Permanent address: Advanced Light Source (formerly Center for X-Ray Optics), LBL.

5. Photoelectron Spectroscopy and Electronic Structure of Heavy Group IV-VI Diatomics (Publication 9)

L.-S. Wang, B. Niu, Y.T. Lee, D.A. Shirley, and K. Balasubramanian

Vibrationally resolved HeI (584 Å) photoelectron spectra of the heavy group IV-VI diatomics SnSe, SnTe, PbSe, and PbTe were obtained with a new high-temperature molecular beam source. Ionization potentials and spectroscopic constants are reported for all the ionic states observed. Relativistic complete active-space multi-configuration self-consistent field (MCSCF) followed by multireference singles + doubles relativistic configuration-interaction (CI) calculations, which included up to 200,000 configurations, were made on both the neutral diatomics and their positive ions. Ionization potentials and spectroscopic constants were calculated and were in good agreement with the experimentally measured values. Relativistic CI potential energy curves were calculated for all the neutral ground states and the ionic states involved.

Relativistic effects were shown to play an important role in these heavy diatomics. The $2\sigma_{1/2}^+$ and $2\pi_{1/2}$ states for all four molecular ions showed avoided curve crossings, which resulted in pronounced shoulders in the $\Omega = 1/2$ potential energy curves of PbTe^+ . Experimentally, autoionization transitions were also observed for the PbTe^+ spectrum. The importance of the relativistic effect and chemical bonding in the heavy diatomics is discussed.

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6. High-Resolution Photoelectron Spectroscopy of Clusters of Group V Elements (Publication 7)

L.-S. Wang, B. Niu, Y.T. Lee, and D.A. Shirley

High-resolution HeI (580 Å) photoelectron spectra of As_2 , As_4 , and P_4 were obtained with a newly built high-temperature molecular beam source. Vibrational structure was resolved in the photoelectron spectra of the three cluster species. The Jahn-Teller effect is discussed for the $2E$ and $2T_2$ states of P_4^+ and As_4^+ . As a result of the Jahn-Teller effect, the $2E$ state splits into two bands, and the $2T_2$ state splits into three bands, in combination with the spin-orbital effect. It was observed that the n_2 normal vibrational mode was involved in the vibronic interaction of the $2E$ state, while both the n_2 and n_3 modes were active in the $2T_2$ state.

7. Molecular Beam Photoelectron Spectroscopy of Allene (Publication 8)

Z.Z. Yang,[†] L.-S. Wang, Y.T. Lee, D.A. Shirley, S.Y. Huang, and W.A. Lester, Jr.

The high-resolution HeI (584 Å) photoelectron spectrum of allene rotationally cooled in a seeded supersonic molecular beam has been measured. Vibrational structure was completely resolved in the first band (X^2E), which involved a strong Jahn-Teller effect. A series of *ab initio* double-zeta MCSCF calculations were carried out for the ground state, and a twist angle of 50° was derived for the ground ionic state. Vibrational fine structure was resolved for the first excited ionic state (A^2E) and was assigned to combinations of two symmetric vibrations, $\nu_2(a_1)$, and $\nu_3(a_1)$ with vibrational frequencies of $1320(6)\text{ cm}^{-1}$ and $1030(6)\text{ cm}^{-1}$, respectively.

[†]Permanent address: Institute of Theoretical Chemistry, Jilin University, Changchun, People's Republic of China.

8. Electronic Structure and Chemical Bonding of the First-Row Transition Metal Dichlorides, MnCl_2 , NiCl_2 , and ZnCl_2 : A High-Resolution Photoelectron Spectroscopic Study (Publication 10)

L.-S. Wang, B. Niu, Y.T. Lee, and D.A. Shirley

High-resolution HeI (584 Å) photoelectron spectra of ZnCl_2 , MnCl_2 , and NiCl_2 were measured using a high-temperature supersonic molecular beam source. In ZnCl_2 , vibrational structures were resolved, and spectroscopic constants were derived for the observed molecular ion states. A single n_1 vibrational progression was observed for the C^2S_g^+ states of ZnCl_2^+ . A Franck-Condon factor calculation allowed us to obtain a Zn-Cl equilibrium bond length increase of 0.09(5) Å and a n_1 vibrational frequency of 290(8) cm^{-1} . For the open-shell molecules, MnCl_2 and NiCl_2 , no vibrational structure could be resolved because of their very low bending frequencies. Transitions from the ligand orbital and metal d-orbital ionizations were clearly resolved, with those of the d orbitals having considerably narrower band widths. Even though many final states are expected for ionization of the open-shell d orbitals, only a few states were observed. This was explained in MnCl_2 by the one-electron spin-selection rule: $S_f = S_i \pm 1/2$. Besides the spin-selection rule, a propensity toward high spin was proposed to account for the spectrum of NiCl_2 . From the metal d-orbital and ligand orbital splittings, the degree of covalent bonding was inferred to be in the order of: $\text{MnCl}_2 > \text{NiCl}_2 > \text{ZnCl}_2$.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. M.N. Piancastelli, T.A. Ferrett, D.W. Lindle, L.J. Medhurst, P.A. Heimann, S.H. Liu, and D.A. Shirley, "Resonant Processes Above the Carbon 1s Ionization Threshold in Benzene and Ethylene," *J. Chem. Phys.* **90**, 3004 (1989); LBL-22548.
2. K.T. Leung, X.S. Zhang, and D.A. Shirley, "Adsorption and Surface Reactions of H_2S and SO_2 on Cu(100) Studied by Electron Energy Loss Spectroscopy," *J. Phys. Chem.* **93**, 6164 (1989); LBL-25552.
3. D.A. Shirley, L.J. Terminello, and C.C. Bahr, "Reply to 'Investigation with Low-Energy Electron Diffraction of the Adsorbate-Induced Metal Relaxations in the Cu(100)-(2 × 2)-S Surface Structure'," *Phys. Rev. B* **39**, 8003 (1989); LBL-25838.

4. L.-S. Wang, B. Niu, Y.T. Lee, and D.A. Shirley, "Vibrational Spectra of Se_2^+ and Te_2^+ in Their Ground States," *Chem. Phys. Lett.* **158**, 297 (1989); LBL-26993.

LBL Reports

5. L.J. Medhurst, A. Schach von Wittenau, R.D. van Zee, J. S. Zhang, S.H. Liu, and D.A. Shirley, "Threshold Photoelectron Spectrum of the Argon 3s Satellites," LBL-27468.
6. L.-S. Wang, J.E. Reutt-Robey, B. Niu, Y.T. Lee, and D.A. Shirley, "High Temperature and High Resolution UV Photoelectron Spectroscopy Using Supersonic Molecular Beams," LBL-27583.
7. L.-S. Wang, B. Niu, Y.T. Lee, and D.A. Shirley, "High Resolution Photoelectron Spectroscopy of Clusters of Group V Elements," LBL-27584.
8. Z.Z. Yang, L.-S. Wang, Y.T. Lee, D.A. Shirley, S.Y. Huang, and W.A. Lester, Jr., "Molecular Beam Photoelectron Spectroscopy of Allene," LBL-27633.
9. L.-S. Wang, B. Niu, Y.T. Lee, D.A. Shirley, and K. Balasubramanian, "Photoelectron Spectroscopy and Electronic Structure of Heavy Group IV-VI Diatomics," LBL-27699.
10. L.-S. Wang, B. Niu, Y.T. Lee, and D.A. Shirley, "Electronic Structure and Chemical Bonding of the First Row Transition Metal Dichlorides, MnCl_2 , NiCl_2 , and ZnCl_2 : A High Resolution Photoelectron Spectroscopic Study," LBL-27925.
11. P.A. Heimann, F. Senf, W. McKinney, M. Howells, R.D. van Zee, L.J. Medhurst, T. Lauritzen, J. Chin, J. Meneghetti, W. Gath, H. Hogrefe, and D.A. Shirley, "High-Resolution Results from the LBL 55-Meter SGM at SSRL Near the K-Edge of Carbon and Nitrogen," LBL-28744.

Invited Talks

12. D.A. Shirley, "A Photoelectron Spectroscopist's Plans for the Advanced Light Source," Pohang Light Source Workshop, Pohang, Republic of Korea, Aug. 13, 1989.
13. D.A. Shirley, "Synchrotron Radiation Based Photoemission from Atoms, Molecules, and Solids," Daeduk Science Town, Republic of Korea, Aug. 20, 1989.
14. D.A. Shirley, "Synchrotron Radiation Based Photoemission," Department of Chemistry, Seoul National University, Seoul, Republic of Korea, Aug. 22, 1989.
15. D.A. Shirley, "Advanced Light Sources," plenary invited talk at ACOLS (Australian Conference on Optics, Lasers, and Spectroscopy), Adelaide University, Australia, Sept. 27, 1989.
16. D.A. Shirley, "Surface Structures from Energy-Dependent Photoelectron Diffraction," FOM Amsterdam, Nov. 6, 1989.

Crossed Molecular Beams*

Yuan T. Lee, Investigator

INTRODUCTION

The major thrust of this research project is to elucidate detailed dynamics of simple elementary reactions that are theoretically important and to unravel the mechanism of complex chemical reactions or photochemical processes that play important roles in many macroscopic processes. Molecular beams of reactants are used to study individual reactive encounters between molecules or to monitor photodissociation events in a collision-free environment. Most of the information is derived from measurement of the product fragment energy, angular, and state distributions. Recent activities are centered on the mechanisms of elementary chemical reactions involving oxygen atoms with unsaturated hydrocarbons, the dynamics of endothermic substitution reactions, the dependence of the chemical reactivity of electronically excited atoms on the alignment of excited orbitals, the primary photochemical processes of polyatomic molecules, intramolecular energy transfer of chemically activated and locally excited molecules, the energetics of free radicals that are important to combustion processes, the infrared-absorption spectra of carbonium ions and hydrated hydronium ions, and bond-selective photodissociation through electric excitation.

1. Measurement of the Perpendicular Rotational-Tunneling Spectrum of the Water Dimer by Tunable Far-Infrared Laser Spectroscopy in a Planar Supersonic Jet (Publication 2)

K.L. Busarow, R.C. Cohen, G.A. Blake, K.B. Laughlin, Y.T. Lee, and R.J. Saykally

Fifty-six transitions from the $K = 1$ lower $\rightarrow K = 2$ lower tunneling-rotation band of water dimer have been measured and assigned at 22 cm^{-1} by direct absorption spectroscopy in a continuous-wave planar supersonic jet expansion using a tunable far-infrared laser spectrometer. Two different models were used to fit the data, and several spectroscopic constants were determined for the upper and lower states. This work supports the local internal-axis-method model recently proposed by Coudert and Hougen

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for the hydrogen bond tunneling dynamics of the water dimer. This model includes four different tunneling motions, all of which contribute to the observed tunneling splittings. This is the most complicated hydrogen bonded system considered to be well understood at this time, at least in the lowest few K states.

2. Vibrational Spectra of Se_2^+ and Te_2^+ in their Ground States (Publication 3)

L. Wang, B. Niu, Y.T. Lee, and D.A. Shirley

Vibrational resolved photoelectron spectra of Se_2^+ and Te_2^+ in their ground states were measured using a newly constructed high-temperature supersonic molecular-beam source. Ionization potentials and fundamental spectroscopic constants for the molecular ions were observed.

3. UV Photodissociation and Thermochemistry of $\text{CH}_2\text{BrCH}_2\text{I}$, $\text{CF}_2\text{BrCF}_2\text{I}$, and $\text{CF}_2\text{ICF}_2\text{I}$ (Publication 4)

G.M. Nathanson, T.K. Minton, S.F. Shane, and Y.T. Lee

Using photofragment translational spectroscopy, we have monitored the dissociation of $\text{CH}_2\text{BrCH}_2\text{I}$ at 248, 266, and 308 nm, and $\text{CF}_2\text{BrCF}_2\text{I}$ and $\text{CF}_2\text{ICF}_2\text{I}$ at 308 nm. The primary fragments are $\text{I}(^2\text{P}_{3/2})$ and $\text{I}(^2\text{P}_{1/2})$ and the corresponding haloethyl radicals. The $\text{I}(^2\text{P}_{3/2})$ contribution decreases upon fluorination, but it is dominant for $\text{CH}_2\text{BrCH}_2\text{I}$ at 308 nm. The electronic absorption dipole lies roughly along the C-I bond axis in every case. Stable $\text{CF}_2\text{CF}_2\text{Br}$ and $\text{CF}_2\text{CF}_2\text{I}$ radicals can be readily generated through photodissociation of the parent compounds, while stable $\text{CF}_2\text{CH}_2\text{Br}$ could not be unambiguously observed. Upper limits to the reaction enthalpy at 0 K for $\text{CF}_2\text{ICF}_2\text{Br}(\text{I}) \rightarrow \text{C}_2\text{F}_4 + \text{I} + \text{Br}(\text{I})$ are $75 \pm 1(59 \pm 1)$ kcal/mol. The time-of-flight spectra and related data suggest that there is a barrier to decomposition for $\text{CF}_2\text{CF}_2\text{I} \rightarrow \text{C}_2\text{F}_4 + \text{I}$ that exceeds the C-I bond energy in the radical.

4. Infrared Spectroscopy of the Pentacoordinated Carbonium Ion C_2H_7^+ (Publication 5)

L.I. Yeh, J.M. Price, and Y.T. Lee

The infrared spectrum of C_2H_7^+ has been obtained from 2500 to 4200 cm^{-1} . The apparatus consists of a tandem mass spectrometer with a radio-frequency octupole ion trap. After initial mass selection of the C_2H_7^+ in a sector

magnet, the $C_2H_7^+$ is spectroscopically probed by using a two-color laser scheme while being trapped under ultrahigh-vacuum conditions. The first laser is scanned from 2500 to 4200 cm^{-1} and excites a C-H stretching vibration. The second laser is a continuous-wave CO_2 laser and is used to dissociate the vibrationally excited parent ions through a multiphoton process. The fragment ion $C_2H_5^+$ is detected by using a quadrupole mass spectrometer. Two sets of spectral features were studied that showed different dependences on the backing pressure in the ion source, on the mixing ratio of hydrogen to ethane, and on the presence or absence of the second laser. Arguments are presented that the two groups of bands can be assigned to the classical and bridging structures of $C_2H_7^+$.

5. Observation of Internal Rotation in the $NH_4^+(NH_3)_4$ Ionic Cluster (Publication 6)

J.M. Price, M.W. Crofton, and Y.T. Lee

The gas-phase infrared vibration-rotation spectrum of the tetra-ammoniated ammonium ion, $NH_4^+(NH_3)_4$, was obtained from 2600 to 3500 cm^{-1} using a multiphoton excitation technique. Cold, mass-selected $NH_4^+(NH_3)_4$ ionic clusters were held in an octupole ion trap while they interacted with a pulsed, tunable infrared laser. Absorption of a single photon of infrared light promoted the ion to a discrete energy level from which a second photon could excite the system over the dissociation threshold. Spectra were obtained by using a second stage of mass selection to monitor the number of smaller massed daughter ionic clusters produced as a function of the laser wavelength.

The spectrum for $NH_4^+(NH_3)_4$ revealed features that could be assigned to transitions arising from the vibrational motion of both the NH_4^+ ionic core of the system and the NH_3 solvent molecules. A particularly striking observation was that of a series of subbands spaced by 12.6 cm^{-1} , superimposed on the band centered at 3420 cm^{-1} . This band was assigned to an antisymmetric stretch of the solvent NH_3 's analogous to ν_3 in free ammonia. The prominent subbands in this transition were assigned to $K = \pm 1$ transitions arising from the internal rotation of the ammonia molecules about their local C_3 axes. A fairly good fit of the spectrum could be obtained by modeling the system as an ammonia molecule attached to a "wall" oriented with the C_3 axis perpendicular to the surface. Internal rotation in an ionic cluster system had not been observed previously.

6. Vibrational Spectroscopy of the Hydrated Hydronium Cluster Ions, $H_3O^+(H_2O)_n$ ($n = 1, 2, 3$) (Publication 9)

L.I. Yeh, M. Okumura, J.D. Myers, J.M. Price, and Y.T. Lee

The gas-phase infrared spectra of the hydrated hydronium cluster ions, $H_3O^+(H_2O)_n$ ($n = 1, 2, 3$) have been observed from 3550 to 3800 cm^{-1} . The new spectroscopic method developed for this study is a two-color scheme consisting of a tunable continuous-wave infrared laser with 0.5 cm^{-1} resolution used to excite the O-H stretching vibrations and a continuous-wave CO_2 laser that dissociates the vibrationally excited cluster ion through a multiphoton process. The apparatus is a tandem mass spectrometer with a radio-frequency ion trap that utilizes the following scheme: the cluster ion to be studied is first mass selected; spectroscopic interrogation then occurs in the radio frequency ion trap; finally, a fragment ion is selected and detected using ion counting techniques. The vibrational spectra obtained in this manner are compared with that taken previously using a weakly bound H_2 "messenger." A spectrum of $H_7O_3^+$ taken using a neon messenger is also presented. *Ab initio* structure and frequency predictions by Remington and Schaefer are compared with the experimental results.

7. Crossed Molecular Beam Study of the Reaction $O(^3P) + C_2H_2$ (Publication 10)

A.M. Schmoltner, P.M. Chu, and Y.T. Lee

The reaction between ground-state atomic oxygen and acetylene was studied using the crossed molecular beam method with an average collision energy of 6 kcal/mole. The two major primary reaction channels are (a) formation of CH_2 and CO , and (b) formation of $HCCO$ and H . Product angular distributions and time-of-flight spectra were measured, and the translational energy release was determined for each channel. The reaction proceeds primarily on the triplet surface through a long-lived intermediate. For both channels the translational energy distributions were found to peak at about 30% of the total available energy, indicating the existence of an exit-channel barrier in each case. The branching ratio between channels (a) and (b) was found to be 1.4 ± 0.5 .

8. State-Selective Ionization of Nitrogen in the $X^2\Sigma_g^+$ $v_+ = 0$ and $v_+ = 1$ States by Two-Color (1 + 1) Photon Excitation Near Threshold (Publication 11)

T. Trickl, E. Cromwell, Y.T. Lee, and A.H. Kung

Efficient generation of $N_2^+ X^2\Sigma_g^+$ ($v_+ = 0, 1$) is demonstrated by an extreme-ultraviolet + visible (1 + 1) photon-excitation scheme. The $c'_4 1\Sigma_g^+$ ($v' = 0, 1$) Rydberg states are used as intermediates. The N_2 molecules are ionized near the $v_+ = 0$ and $v_+ = 1$ ionization thresholds. The autoionizing $nd\delta_g 1\Delta_g$ Rydberg series with the rotational quantum numbers $N = 4, 5$, and 6 (in the limit of 1 uncoupling) are observed for the first time. Extrapolation of the $N = 4$ series yields an ionization energy of N_2 of $125,666.959(67) \text{ cm}^{-1}$.

9. Crossed Molecular Beam Study of the Reaction $O(^3P) + C_2H_4$ (Publication 12)

A.M. Schmoliner, P.M. Chu, R.J. Brudzynski, and Y.T. Lee

The reaction between ground-state atomic oxygen and ethylene was studied under single-collision conditions using the crossed molecular beam method. At an average collision energy of about 6 kcal/mole, the two major primary reaction channels are (a) the formation of CH_3 and CHO , and (b) the formation of C_2H_3O and H . Product angular distributions and time-of-flight spectra were measured, and the translational energy release was determined for each channel. The observed results and calculated potential energy surfaces suggest that after the addition of $O(^3P)$ to ethylene, forming a triplet diradical, channel (a) occurs by way of intersystem crossing to the singlet state, 1,2-H migration and subsequent C-C bond rupture, whereas channel (b) proceeds mostly through the direct dissociation of the intermediate triplet diradical, except for a small contribution from H-atom elimination of the singlet acetaldehyde intermediate.

10. Photodissociation of Vinyl Bromide and the Heat of Formation of the Vinyl Radical (Publication 13)

A.M. Wodtke, E.J. Hints, J. Somorjai, and Y.T. Lee

We have performed measurements of the translational energy distributions and anisotropy parameters of the photodissociation products of vinyl bromide at 193 nm. Br-atom and HBr elimination were observed, with a branching ratio between the two channels of 1.28 ± 0.05 . Both processes occurred with a large release of translational energy, an average of about 2.0 eV for the

Br-atom channel and somewhat less for HBr elimination. The maximum release of translational energy for $Br + C_2H_3$ formation led to an upper limit of $77 \pm 3 \text{ kcal/mol}$ to $D_0(C_2H_3-Br)$, from which an upper limit to the heat of formation of the vinyl radical, $71 \pm 3 \text{ kcal/mol}$, was derived. This result was used to re-examine crossed molecular beams data relevant to the determination of the vinyl radical heat of formation. A metastable state of C_2H_3 observed in the photodissociation of vinyl bromide was interpreted as the formation of $C_2H_3(\tilde{A}^2A)$.

11. Molecular Beam Studies of Hot Atom Chemical Reactions: Reactive Scattering of Energetic Deuterium Atoms (Publication 14)

R.E. Continetti, B.A. Balko, and Y.T. Lee

A brief review of the application of the crossed molecular beams technique to the study of hot-atom chemical reactions in the last twenty years is given. Specific emphasis is placed on recent advances in the use of photolytically produced energetic deuterium atoms in the study of the fundamental elementary reaction $D + H_2 \rightarrow DH + H$ and the substitution reaction $D + C_2H_2 \rightarrow C_2HD + H$. Recent advances in UV laser and pulsed molecular beam techniques have made the detailed study of hydrogen-atom reactions under single-collision conditions possible.

12. Infrared Spectra of the Solvated Hydronium Ion. Vibrational Predissociation Spectroscopy of Mass-Selected $H_3O^+ \cdot (H_2O)_n \cdot (H_2)_m$ (Publication 16)

M. Okumura, L.J. Yeh, J.D. Myers, and Y.T. Lee

Infrared spectra of the mass-selected clusters $H_3O^+ \cdot (H_2O)_n \cdot (H_2)$ and $H_3O^+ \cdot (H_2)_n$ ($n = 1, 2$, and 3) were observed by vibrational predissociation spectroscopy. The clusters were mass-selected and then trapped in a radio frequency ion trap. Cluster dissociation by loss of H_2 followed excitation of OH or H_2 stretches. Spectra were recorded by detecting fragment ions as a function of laser frequency. From spectra of $H_3O^+ \cdot (H_2O)_n \cdot (H_2)$, we were able to determine the spectrum of the hydrated hydronium ion $H_3O^+ \cdot (H_2O)_n$, because the H_2 formed weak complexes with the hydrates. Spectra in the OH stretching region (3000 to 4000 cm^{-1}) were observed at a resolution of 1.3 cm^{-1} for clusters $n = 1, 2$, and 3. The structure of the clusters and the perturbing effect of the H_2 were inferred from a comparison with recent unpublished *ab initio* vibrational frequencies calculated by Remington and Schaefer. Observation of the hydrogen-bonded OH stretch

in $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$ at 267 cm^{-1} confirmed the assignment of the low resolution spectrum obtained by Schwarz. Infrared spectra of the hydronium ion solvated by H_2 were also reported. In the clusters $\text{H}_3\text{O}^+(\text{H}_2)_n$ ($n = 1, 2$, and 3), all OH and H_2 stretching vibrations were observed. In several bands of $\text{H}_3\text{O}^+(\text{H}_2)$, rotational structure was partially resolved, with the resolution limited by the laser linewidth of 0.8 cm^{-1} .

13. The Translational Energy Dependence of the $\text{F} + \text{C}_2\text{H}_4 \rightarrow \text{H} + \text{C}_2\text{H}_3\text{F}$ Reaction Cross Section Near Threshold (Publication 17)

G.N. Robinson, R.E. Continetti, and Y.T. Lee

We have carried out crossed molecular beam studies of the substitution reaction $\text{F} + \text{C}_2\text{H}_4 \rightarrow \text{H} + \text{C}_2\text{H}_3\text{F}$ in the collision energy range $0.8\text{--}2.5\text{ kcal/mol}$ using a velocity-selected F-atom beam. The relative substitution cross section is found to decrease with increasing collision energy, indicating that if there is a potential energy barrier to F-atom addition to C_2H_4 , it is much less than 0.8 kcal/mol and that the transition state for addition occurs early along the reaction coordinate. These results agree well with *ab initio* calculations. Although the product translational energy distributions are similar to those obtained from earlier work at higher collision energies, the $\text{C}_2\text{H}_3\text{F}$ angular distributions suggest that a wider range of reactant approach geometries leads to products at lower energies.

14. Molecular Beam Photoelectron Spectroscopy of Allene (Publication 18)

Z.Z. Yang, L.S. Wang, Y.T. Lee, D.A. Shirley, S.Y. Huang, and W.A. Lester, Jr.

The high-resolution photoelectron spectrum of allene rotationally cooled in a supersonic molecular beam has been measured. Analysis of the first part of the 1^2E band based on a simple anharmonic potential model for the torsional vibration near equilibrium geometry yielded the force constant $k = 16921 \pm 20\text{ cm}^{-1}$, the vibrational frequency $\nu_4(b_1) = 806 \pm 8\text{ cm}^{-1}$, and the twist angle $\theta = 49 \pm 3^\circ$ for the ground ionic state. A series of *ab initio* double-zeta multiconfiguration self-consistent-field (MCSCF) calculations for the two low-lying ionic states of allene gave a good description of the first band. Three vibrational progressions in the second band were resolved and assigned to the three totally symmetric vibrations $\nu_1(a_2)$, $\nu_2(a_1)$, and $\nu_3(a_1)$, with vibrational frequencies 2597 cm^{-1} , 1315 cm^{-1} , and 102 cm^{-1} , respectively.

15. High-Resolution Photoelectron Spectroscopy of Clusters of Group V Elements (Publication 19)

L.-S. Wang, B. Niu, Y.T. Lee, and D.A. Shirley

High-resolution HeI ($580\text{ \AA}$) photoelectron spectra of As_2 , As_4 , and P_4 were obtained with a newly built high-temperature molecular beam source. Vibrational structure was resolved in the photoelectron spectra of the three cluster species. The Jahn-Teller effect is discussed for the ^2E and $^2\text{T}_2$ states of P_4^+ and As_4^+ . As a result of the Jahn-Teller effect, the ^2E state splits into two bands, and the $^2\text{T}_2$ state splits into three bands, in combination with the spin-orbit effect. It was observed that the ν_2 normal vibrational mode was involved in the vibronic interaction of the ^2E state, while both the ν_2 and ν_3 modes were active in the $^2\text{T}_2$ state.

16. Molecular Beam Studies of the Photodissociation of Benzene at 193 and 248 nm (Publication 20)

A. Yokoyama, X. Zhao, E.J. Hints, R.E. Continetti, and Y.T. Lee

The photodissociation processes of benzene following excitation at 193 and 248 nm have been studied by molecular beam photofragmentation translational spectroscopy. When benzene was excited to the 1B_{1u} state by absorption at 193 nm, dissociation occurred through three primary channels, $\text{C}_6\text{H}_5 + \text{H}$ (80%), $\text{C}_6\text{H}_4 + \text{H}_2$ (16%), and $\text{C}_5\text{H}_3 + \text{CH}_3$ (4%), following internal conversion to the vibrationally excited ground state. When benzene was excited to the 1B_{2u} state at 248 nm, two primary dissociation channels, $\text{C}_6\text{H}_4 + \text{H}_2$ (96%) and $\text{C}_5\text{H}_3 + \text{CH}_3$ (4%), were observed. Photodissociation to produce two C_3H_3 was induced by two-photon absorption of benzene at both 193 and 248 nm. Numerous secondary photodissociation processes of the primary photoproducts were also observed at both 193 and 248 nm.

17. Photodissociation of 2-Bromoethanol and 2-Chloroethanol at 193 nm (Publication 21)

E.J. Hints, X. Zhao, and Y.T. Lee

2-bromoethanol and 2-chloroethanol were photodissociated in a molecular beam at 193 nm. Only one primary reaction channel was observed, elimination of the halogen atom, with an average translational energy release of 33 kcal/mol . In the case of 2-bromoethanol, some of the $\text{C}_2\text{H}_4\text{OH}$ partner fragment survived, and some underwent secondary dissociation to produce C_2H_4 and OH. The

surviving $\text{C}_2\text{H}_4\text{OH}$ contained up to 43 kcal/mol of internal energy, far more than the expected $\text{C}_2\text{H}_4\text{-OH}$ bond energy of ~ 28 kcal/mol. The initial C-Br recoil occurs with a large exit impact parameter and leaves most of the internal energy in $\text{C}_2\text{H}_4\text{OH}$ rotation, creating rotationally metastable fragments. The angular distributions of the secondary C_2H_4 and OH products were strongly forward-backward peaked with respect to the primary ($\text{C}_2\text{H}_4\text{OH}$) velocity vector, consistent with the decay of a long-lived complex in which the total angular momentum is perpendicular to the velocity vector and mainly carried away as orbital angular momentum. This effect is analogous to that observed in the decay of similar long-lived complexes in crossed molecular beams experiments.

18. High-Temperature and High-Resolution UV Photoelectron Spectroscopy Using Supersonic Molecular Beams (Publication 22)

L.-S. Wang, J.E. Reutt-Robey, B. Niu, Y.T. Lee, and D.A. Shirley

A high-temperature molecular beam source with electron-bombardment heating has been built for high-resolution photoelectron spectroscopic studies of high-temperature species and clusters. This source has the advantages of (1) producing an intense, continuous, seeded molecular beam, and (2) eliminating the interference of the heating mechanism from the photoelectron measurement. Coupling the source with our hemispherical electron-energy analyzer, we can obtain very high-resolution HeI α (584 Å) photoelectron spectra of high-temperature species. Vibrationally resolved photoelectron spectra of PbSe, As₂, As₄, and ZnCl₂ are shown to demonstrate the performance of the new source.

19. Photoelectron Spectroscopy and Electronic Structure of Heavy Group IV–VI Diatomics (Publication 23)

L.-S. Wang, B. Niu, Y.T. Lee, D.A. Shirley, and K. Balasubramanian

Vibrationally resolved HeI (584 Å) photoelectron spectra of the heavy group IV–VI diatomic SnSe, SnTe, PbSe, and PbTe were obtained with a new high-temperature molecular beam source. Ionization potentials and spectroscopic constants are reported for all the ionic

states observed. Relativistic complete active-space MCSCF followed by multireference singles + doubles relativistic configuration-interaction (CI) calculations, which included up to 200,000 configurations, were made on both the neutral diatomics and their positive ions. Ionization potentials and spectroscopic constants were calculated and were in good agreement with the experimentally measured values. Relativistic CI potential energy curves were calculated for all the neutral ground states and the ionic states involved. Relativistic effects were shown to play an important role in these heavy diatomics. The $^2\Sigma_{1/2}^+$ and $^2\Pi_{1/2}$ states for all four molecular ions showed avoided curve crossings, which resulted in pronounced shoulders in the $\Omega = 1/2$ potential energy curves of PbTe^+ . Experimentally, autoionization transitions were also observed for the PbTe^+ spectrum. The importance of the relativistic effect and chemical bonding in the heavy diatomics are discussed.

20. Tunable Far-Infrared Laser Spectroscopy of van der Waals Bonds: The Intermolecular Stretching Vibration and Effective Radial Potentials for Ar–H₂O (Publication 24)

R.C. Cohen, K.L. Busarow, Y.T. Lee, and R.J. Saykally

Measurements of the fundamental van der Waals stretching vibration $\Sigma(0_{00}, v_s = 1) \leftarrow \Sigma(0_{00}, v_s = 0)$ of Ar–H₂O [$\nu_0 = 907,322.08(94)$ MHz] and a transition from the lowest excited internal rotor state $\Sigma(1_{01}, v_s = 0)$ to the $\Sigma(1_{01}, v_s = 1)$ level [$\nu_0 = 1,019,239.4(1.0)$ MHz] are presented. A simultaneous rotational analysis of the new stretching data with the internal rotor bands observed by us previously,¹ including the effects of coriolis interactions, provides experimental evidence of the new assignment of the internal rotor transitions suggested by Hutson in the accompanying paper. Fits to the rotational term values for the $v_s = 0$ states are used to derive effective radial potential energy surfaces for each of the Σ internal rotor states. The results show the well depth (153.4 cm^{-1}) of the effective radial potential for the $\Sigma(1_{01}, v_s = 0)$ level to be approximately 25 cm^{-1} deeper than that for the $\Sigma(0_{00}, v_s = 0)$ ground state of the complex, indicating that the former is stabilized considerably more by the anisotropic intermolecular potential energy surface than is the ground state.

1. R.C. Cohen, K.L. Busarow, K.B. Laughlin, G.A. Blake, M. Havenith, Y.T. Lee, and R.J. Saykally, *J. Chem. Phys.* **89**, 4494 (1988).

21. Dynamics of H₂ Elimination from 1,4-Cyclohexadiene (Publication 25)

E.F. Cromwell, D.-J. Liu, M.J.J. Vrakking, A.H. Kung, and Y.T. Lee

The dynamics of H₂ elimination from 1,4-cyclohexadiene (CHDN), dissociated with 212-nm light, have been studied by state-specific probing of the H₂ product via 1 + 1 resonance-enhanced multiphoton ionization using a transform-limited vuv laser system. The quantum-state distributions, the translational energy distribution, and the Doppler profiles were measured, giving a "rotational temperature" of ≈ 1600 K, a "vibrational temperature" of ≈ 4000 K, and a translational energy of ≈ 30 kcal/mole for H₂. Anisotropy in the Doppler profiles indicates that the H₂'s velocity vector is aligned parallel to its rotational angular momentum vector.

22. Work in Progress

Substitution reactions of energetic D atoms with unsaturated hydrocarbons, especially $D + C_2H_2 \rightarrow C_2HD + D$, are making good progress. Reactions with C₂H₄ and C₆H₆ will follow.

The intermolecular energy transfer of very highly internally excited molecules is now focused on the condensation processes on a cold surface. The key question to be answered is whether the rotational energy or the vibrational energy is more effective in reducing the sticking coefficient of very highly internally excited molecules.

The photodissociation of NO₃ radicals as a function of excitation wavelength is now under extensive investigation, in collaboration with Harold Johnston's group. The branching ratio of NO + O₂ and NO₂ + O channels are being precisely determined.

In order to understand the effect of orbital alignment in the reaction of electronically excited Ba atoms, we are now investigating the chemi-ionization process that produces various ions. These measurements will elucidate the details of complex multi-crossings of the potential energy surfaces.

Solvation of metal ions is now under investigation using IR absorption spectroscopy. The dynamics of the removal of solvent molecules through selective vibrational excitation of NH₄⁺(H₂O)(NH₃)₂ is expected to provide us with some information on intramolecular relaxation.

High-resolution overtone excitation of benzene for $v = 0 \rightarrow v = 2$ reveals that these transitions have extremely narrow lines. More than one hundred transitions were resolved in each of the 21 transitions observed previously

with 1 cm⁻¹ resolution. We are now trying to obtain $v = 0 \rightarrow v = 3$ transitions using transform-limited lasers.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. T. Trickl, M.J.J. Vrakking, E. Cromwell, Y.T. Lee, and A.H. Kung, "Ultrahigh-Resolution (1 + 1) Photoionization Spectroscopy of KrI: Hyperfine Structures, Isotope Shifts and Lifetimes for the $n = 5, 6, 7$ 4p⁵ns Rydberg States," *Phys. Rev. A* **39**, 2948 (1989); LBL-25787.
2. K.L. Busarow, R.C. Cohen, G.A. Blake, K.B. Laughlin, Y.T. Lee, and R.J. Saykally, "Measurement of the Perpendicular Rotational-Tunneling Spectrum of the Water Dimer by Tunable Far Infrared Laser Spectroscopy in a Planar Supersonic Jet," *J. Chem. Phys.* **90**, 3937 (1989); LBL-26174.
3. L. Wang, B. Niu, Y.T. Lee, and D.A. Shirley, "Vibrational Spectra of Se₂⁺ and Te₂⁺ in their Ground States," *Chem. Phys. Lett.* **158**, 297 (1989); LBL-26993.
4. G.M. Nathanson, T.K. Minton, S.F. Shane, and Y.T. Lee, "UV Photodissociation and Thermochemistry of CH₂BrCH₂I, CF₂BrCF₂I, and CF₂ICF₂I," *J. Chem. Phys.* **90**, 6157 (1989); LBL-26709.
5. L.I. Yeh, J.M. Price, and Y.T. Lee, "Infrared Spectroscopy of the Pentacoordinated Carbonium Ion C₂H₇⁺," *J. Am. Chem. Soc.* **111**, 5597 (1989); LBL-26767.
6. J.M. Price, M.W. Crofton, and Y.T. Lee, "Observation of Internal Rotation in the NH₄⁺(NH₃)₄ Ionic Cluster," *J. Chem. Phys.* **91**, 2748 (1989); LBL-27022.
7. E. Cromwell, T. Trickl, Y.T. Lee, and A.H. Kung, "Ultra-Narrow Bandwidth VUV-XUV Laser System," *Rev. Sci. Instrum.* **60**, 2888 (1989); LBL-26041.
8. X. Zhao, R.E. Continetti, A. Yokoyama, E.J. Hints, and Y.T. Lee, "Dissociation of Cyclohexene and 1,4-Cyclohexadiene in a Molecular Beam," *J. Chem. Phys.* **91**, 4118 (1989); LBL-26333.
9. L.I. Yeh, M. Okumura, J.D. Myers, J.M. Price, and Y.T. Lee, "Vibrational Spectroscopy of the Hydrated Hydronium Cluster Ions, H₃O⁺·(H₂O)_n ($n = 1, 2, 3$)," *J. Chem. Phys.* **91**, 7319 (1989); LBL-26708.
10. A.M. Schmoltner, P.M. Chu, and Y.T. Lee, "Crossed Molecular Beam Study of the Reaction O(³P) + C₂H₂," *J. Chem. Phys.* **91**, 5365 (1989); LBL-27287.
11. T. Trickl, E. Cromwell, Y.T. Lee, and A.H. Kung, "State-Selective Ionization of Nitrogen in the X 2Σ_g⁺ v⁺ = 0 and v⁺ = 1 States by Two-Colour (1 + 1) Photon Excitation Near Threshold," *J. Chem. Phys.* **91**, 6006 (1989); LBL-27186.
12. A.M. Schmoltner, P.M. Chu, R.J. Brudzynski, and Y.T. Lee, "Crossed Molecular Beam Study of the Reaction O(³P) + C₂H₄," *J. Chem. Phys.* **91**, 6926 (1989); LBL-27577.

Other Publications

13. A.H. Kung, T. Trickl, E. Cromwell, M.J.J. Vrakking, and Y.T. Lee, "Ultra-high Resolution VUV-XUV Laser: Application to the Hyperfine Study of Krypton," in *Proc. Optical Society Topical Meeting on Short Wavelength Coherent Radiation: Generation and Applications*, North Falmouth, MA, Sept. 26-29, 1988, p. 411; LBL-26760.
14. R.E. Continetti, B.A. Balko, and Y.T. Lee, "Molecular Beam Studies of Hot Atom Chemical Reactions: Reactive Scattering of Energetic Deuterium Atoms," in *Proc. Int. Symp. Near-Future Chemistry in Nuclear Energy Field*, Feb. 15-16, 1989, Japan Atomic Energy Research Institute, Ibaraki-Ken, Japan, 1989, p. 14; LBL-26762.

LBL Reports

15. A.M. Wodtke, E.J. Hints, J. Somorjai, and Y.T. Lee, "Photodissociation of Vinyl Bromide and the Heat of Formation of the Vinyl Radical," *Israel J. Chem.* (in press); LBL-26710.
16. M. Okumura, L.I. Yeh, J.D. Myers, and Y.T. Lee, "Infrared Spectra of the Solvated Hydronium Ion: Vibrational Predissociation Spectroscopy of Mass-Selected $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n(\text{H}_2)_m$," submitted to *J. Phys. Chem.*; LBL-26833.
17. G.N. Robinson, R.E. Continetti, and Y.T. Lee, "The Translational Energy Dependence of the $\text{F} + \text{C}_2\text{H}_4 \rightarrow \text{H} + \text{C}_2\text{H}_3\text{F}$ Reaction Cross Section Near Threshold," submitted to *J. Chem. Phys.*; LBL-27629.
18. Z.Z. Yang, L.S. Wang, Y.T. Lee, D.A. Shirley, S.Y. Huang, and W.A. Lester, Jr., "Molecular Beam Photoelectron Spectroscopy of Allene," submitted to *J. Phys. Chem.*; LBL-27633.
19. L.-S. Wang, B. Niu, Y.T. Lee, and D.A. Shirley, "High Resolution Photoelectron Spectroscopy of Clusters of Group V Elements," submitted to *Physica Scripta*; LBL-27584.
20. A. Yokoyama, X. Zhao, E.J. Hints, R.E. Continetti, and Y.T. Lee, "Molecular Beam Studies of the Photodissociation of Benzene at 193 and 248 nm," submitted to *J. Chem. Phys.*; LBL-27736.
21. E.J. Hints, X. Zhao, and Y.T. Lee, "Photodissociation of 2-Bromoethanol and 2-Chloroethanol at 193 nm," submitted to *J. Chem. Phys.*; LBL-27737.
22. L.-S. Wang, J.E. Reutt-Robey, B. Niu, Y.T. Lee, and D.A. Shirley, "High Temperature and High Resolution UV Photoelectron Spectroscopy Using Supersonic Molecular Beams," submitted to *J. Electron Spectrosc. Rel. Phenom.*; LBL-27583.
23. L.-S. Wang, B. Niu, Y.T. Lee, D.A. Shirley, and K. Balasubramanian, "Photoelectron Spectroscopy and Electronic Structure of Heavy Group IV-VI Diatomics," submitted to *J. Chem. Phys.*; LBL-27699.
24. R.C. Cohen, K.L. Busarow, Y.T. Lee, and R.J. Saykally, "Tunable Far Infrared Laser Spectroscopy of Van der Waals Bonds: The Intramolecular Stretching Vibration and

Effective Radial Potentials for $\text{Ar-H}_2\text{O}$," *J. Chem. Phys.* (in press); LBL-27537.

25. E.F. Cromwell, D.-J. Liu, M.J.J. Vrakking, A.H. Kung, and Y.T. Lee, "Dynamics of H_2 Elimination from 1,4-Cyclohexadiene," submitted to *J. Chem. Phys.*; LBL-28068.

Invited Talks

26. Y.T. Lee, "Ring Opening Photodissociation of Cyclic Organic Molecules," Santa Monica, CA, Jan. 10, 1989.
27. Y.T. Lee, "Dynamics of Elementary Chemical Reactions," Symposium on Frontiers in Chemistry, AAAS Annual Meeting, San Francisco, CA, Jan. 17, 1989.
28. Y.T. Lee, "Chemical Reactions of Energetic H Atoms by the Molecular Beam Technique," International Symposium on Nuclear Energy, Oharai, Japan, Feb. 19, 1989.
29. Y.T. Lee, "Primary Dissociation Processes of Six-Membered Cyclic Hydrocarbons," Japan Atomic Energy Research Institute, Tokai Village, Japan, Feb. 20, 1989.
30. Y.T. Lee, "Rotationally Resolved H_2^+ Infrared Absorption Spectroscopy," AFOSR High Energy Density Materials Contractors Meeting, New Orleans, LA, Mar. 14, 1989.
31. Y.T. Lee, "Dynamics of Elementary Chemical Reactions and Photochemical Processes," C. Emerson Lecture, Department of Chemistry, Emory University, Atlanta, GA, March 21, 1989.
32. Y.T. Lee, "Fossil Fuel Combustion and Environment," Imperial Oil Lecture, Department of Chemical Engineering, University of Western Ontario, London, Ont., Apr. 3, 1989.
33. Y.T. Lee, "Unimolecular Decomposition of Hydrocarbons, Department of Chemical Engineering," University of Western Ontario, London, Ont., Apr. 3, 1989.
34. Y.T. Lee, "Dynamics of Elementary Chemical Reactions and Primary Photochemical Processes," Ontario Laser and Lightwave Research Center, University of Toronto, Toronto, Ont., Apr. 4, 1989.
35. Y.T. Lee, "Reaction of Oxygen Atoms with Unsaturated Hydrocarbons," Ford Motor Company, Dearborn, MI, Apr. 6, 1989.
36. Y.T. Lee, "Dynamics of Elementary Chemical Reactions and Photochemical Processes," Kistiakowsky Lecture, Department of Chemistry, Harvard University, Cambridge, MA, Apr. 20, 1989.
37. Y.T. Lee, "Dynamics and Mechanism of the Dissociation of Energetic Molecules," Symposium on Energetic Molecules in honor of Dr. Richard Miller, Loker Hydrocarbon Institute, University of Southern California, Los Angeles, CA, May 15, 1989.
38. Y.T. Lee, "Reactions of Energetic Deuterium and Barium by the Crossed Molecular Beams Method," International Molecular Beams Symposium, Perugia, Italy, May 29, 1989.
39. Y.T. Lee, "Crossed Molecular Beams Studies of Elementary Chemical Reactions," Department of Chemistry, University of Perugia, Perugia, Italy, May 31, 1989.

40. Y.T. Lee, "Molecular Collisions and Chemical Reactions," 39th Meeting of Nobel Laureates, Lindau, Federal Republic of Germany, June 27, 1989.
41. Y.T. Lee, "Molecular Beam Chemical Kinetics," Director's Distinguished Lecture, Lawrence Livermore National Laboratory, Livermore, CA, Sept. 21, 1989.
42. Y.T. Lee, "Combustion of Fossil Fuel in Modern Society," Sir Run Run Shaw Distinguished Lecture, Shaw College, Chinese University of Hong Kong, Oct. 11, 1989.
43. Y.T. Lee, "IR Spectroscopy of Ammoniated Ammonium Ions," Department of Chemistry, Brookhaven National Laboratory, Upton, NY, Nov. 6, 1989.
44. Y.T. Lee, "Chemical Laser and Laser Chemistry," Haworth Distinguished Lecture, Brookhaven National Laboratory, Upton, NY, Nov. 8, 1989.
45. Y.T. Lee, "Combustion of Fossil Fuel in Human Society," Kaoshiung Technical College, Kaoshiung, Republic of China, Dec. 13, 1989.
46. Y.T. Lee, "Reaction of Ground and Electronically Excited Ba Atoms with Simple Molecules," Annual Meeting of Chinese Chemical Society (Taipei), Fugen University, Taipei, Republic of China, Dec. 16, 1989.
47. Y.T. Lee, "Photodissociation of Chloroethanol and Bromoethanol," Joint Workshop on Molecular Dynamics, Institute for Molecular Sciences (Japan) and Institute of Atomic and Molecular Sciences (Taiwan), Taipei, Republic of China, Dec. 19, 1989.

ATOMIC PHYSICS

High-Energy Atomic Physics*

Harvey Gould, Investigator

INTRODUCTION

The goals of this program are to understand atomic collisions of relativistic ions, to test quantum electrodynamics (QED) and relativistic many-body calculations in the strong Coulomb field of very high atomic number (Z) atoms, and to search for a CP non-conserving electron electric-dipole moment (EDM). Relativistic collisions and high- Z QED experiments can only be carried out with relativistic heavy ions. These experiments are conducted at the Lawrence Berkeley Laboratory's Bevalac.

Recent results include a 500 part-per-million measurement of the energy of the $2^2P_{1/2} - 2^2S_{1/2}$ transition in lithiumlike uranium (U^{89+}). This is an exacting test that challenges new relativistic many-body calculations in the most relativistic, most quantum electrodynamic, and least many-body system available. When the calculations are complete, this measurement will yield a 0.25% determination of the electron self-energy in uranium.

Present activities include measurement of screening-antiscreening effects in relativistic ionization, an attempt to observe a new capture mechanism — electron capture from the production of electron-positron pairs by the motional Coulomb fields of relativistic nuclei passing within atomic distances of each other, and an experiment to set a stringent upper bound on the electron EDM.

1. Work in Progress

A possible failure of quantum electrodynamics (QED) to predict accurate radiative corrections to bound states at (atomic number) $Z = 92$ is not ruled out by its success at

low Z . This is because the largest contribution to the Lamb shift at $Z = 92$ comes from terms in the electron self-energy that are high powers of Z and that are invisible in experiments at low Z . A modest-precision Lamb-shift measurement in high- Z ions such as uranium can provide a powerful test of QED in the high- Z strong-field limit.

Although the most precise experiments have traditionally been performed using hydrogenlike ions, new relativistic many-body calculations now make it feasible to compare QED theory and precision experiments in few-electron uranium. The test of the many-body calculation for such an extremely relativistic system is regarded by many theorists as being at least as significant as the test of QED self-energy.

A high-accuracy measurement of the electron self-energy in uranium is accomplished by measuring the energy of the $2^2P_{1/2} - 2^2S_{1/2}$ transition in three-electron lithiumlike uranium. The self-energy contributes 55 eV out of a total of 280.7 eV for this transition.

In our experiment, a beam of lithiumlike uranium is produced at the LBL Bevalac by stripping uranium ions traveling at roughly half the speed of light. The photons from the $2^2P_{1/2} - 2^2S_{1/2}$ transition are seen Doppler-shifted in the laboratory, and when viewed through a column of argon gas are absorbed as the viewing angle is rotated to an angle that Doppler-shifts the photons above the argon L-edge. The energy of the argon L-edge, the measured beam velocity, and the measured angle between the beam and a well-collimated photon detector determine the energy of the x ray in the rest frame of the lithiumlike uranium.

Data collection was completed, the apparatus was disassembled and removed from the Bevalac, and preliminary data analysis was completed. This experiment was probably the largest and most complex atomic physics experiment ever run at an accelerator in the U.S. The preliminary analysis of the data yielded an accuracy of 0.14 eV, for the 280.7 eV splitting, a factor-of-50 improvement over the result of Munger and Gould.¹

¹C.T. Munger and H. Gould, Phys. Rev. Lett. **57**, 2927 (1986).

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1989 PUBLICATIONS AND REPORTS

Invited Talks

1. N. Claytor, "Electron Impact Ionization of $U^{88+} - U^{91+}$," 16th International Conference on the Physics of Electronic

- and Atomic Collisions, New York, July 28, 1989.
2. J. Schweppe, "Measurement of the Lamb Shift in 3-Electron Uranium," High Energy Physics Seminar, Physics Department, University of Chicago, Dec. 4, 1989; National Institute of Standards and Technology, Gaithersburg, MD, Dec. 7, 1989.

Atomic Physics*

Michael H. Prior, Investigator

INTRODUCTION

This program emphasizes the detailed study of low-energy, highly charged ion-atom collisions, with particular concentration on multiple-electron-transfer processes. A general goal is to perform experiments that describe electron transfer between well-characterized initial and final states so that theoretical predictions can be tested at the finest scale possible. Of particular current interest are double-electron-transfer modes, where the two active electrons may exhibit a correlated behavior; that is, the transfer is not simply the incoherent sum of single-electron-transfer amplitudes. A portion of this program is devoted to carrying out measurements that bear on this question.

In addition to detailed collision studies, this program contains a component devoted to the description and understanding of energy-level structure and decay modes of highly excited atomic systems. Currently this work concentrates on Auger electron spectroscopy, which provides energy-level data for multiply excited states; this work complements photon spectroscopic studies, since levels that Auger decay prominently are usually weak photon emitters. Furthermore, the intensity distribution of the Auger lines provides insight into the states that are populated in the multiple-electron-capture process. The combination of a highly ionized projectile and a neutral atom in close proximity is a highly inverted nonequilibrium system, and thus the detailed study of such collisions is relevant, for example, to the study of nonequilibrium plasmas important to advanced laser concepts.

The approach to this work takes advantage of unique facilities and expertise available at LBL. Currently the studies utilize the high-intensity, highly charged continuous ion beams from the LBL Electron Cyclotron Resonance (ECR) ion sources and beamline facilities. The program benefits substantially from collaborative efforts with colleagues from outside LBL.

1. Auger Electron Emission from Na-Like Fe Ions Excited in Collisions of 170-keV Fe^{17+} on He and Ne (Publication 2)

D. Schneider,[†] M.H. Chen,[†] S. Chantrenne,[†] R. Hutton,[†]
and M.H. Prior

Zero-degree Auger spectroscopy was used to study the excitation and decay of Auger states formed by the transfer of two electrons from He and Ne target atoms to a beam of Fe^{17+} projectile ions. The resulting Na-like Fe^{15+} ions are in an excited state, with both captured electrons predominantly in $n, n' = 3, 3$ or $3, 4$ configurations surrounding the 9-electron Fe^{17+} core (F-like $2p^5$ configuration). The resulting L-shell Auger electron spectra observed when the core vacancy is filled are the first reported from such a highly charged ion excited in a slow atomic collision.

The experiments were performed using ion beams produced by the LBL ECR ion source and the associated atomic-physics beamline facilities. A schematic diagram of the apparatus is shown in Figure 1-1. Figure 1-2 shows an example of some of the observed Auger spectra. The energy scale and intensities in Figure 1-2 have been transformed into the projectile frame ("center of mass"). Figure 1-2(c) was obtained by biasing the gas cell in which the collision occurred to -40 V; this causes a shift to higher energy of all spectral lines that arise from prompt Auger decays inside the cell, leaving unshifted any lines emitted from long-lived excited states that decay after the projectile has left the gas cell. Note that the prominent peak labeled 3 remains unshifted; we have identified this line to be from the Auger decay of the $2p^5 3s 3p^4 D_{7/2}$ level. Quartet terms of Na-like ions are forbidden to Auger decay via the coulomb interaction, which is responsible for all prompt Auger lines, to the extent that total spin is a good quantum number. In the general case, for such highly charged

Figure 1-1. Experimental arrangement for zero-degree electron spectroscopy using a collimated beam from the LBL ECR ion source. The beam passes through the gas cell and 45° parallel-plate analyzer into the Faraday cup. Forward-emitted electrons are deflected by the 45° analyzer into the high-resolution hemispherical instrument. (XBL 891-140)

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Figure 1-2. Fe^{15+} L-Auger spectra following collision of 170-keV Fe^{17+} ions with He and Ne gas targets. The energy scale has been transformed into a frame moving with the projectile. Lines and features indicated in (a) have been identified with the aid of theoretical calculations and photon spectroscopic measurements. The peak labeled 3 does not shift in energy when the gas cell is biased to -40 V (b and c), indicating that it is due to the decay of a metastable state. Part (d) shows a background spectrum from the residual gas pressure of 3×10^{-7} Torr in the target cell chamber. (XBL 904-1220)

systems, spin is not a good quantum number, and one finds the LS doublet and quartet states mixed. However, the state of maximum total angular momentum J in each configuration has no nearby doublet state of the same J and thus approximates a pure quartet state. The $2p^5 3s 3p \ ^4D_{7/2}$ level is also the lowest in energy of the "quartet" system and therefore may not decay by electric-dipole photon emission. The result is that this level has a long lifetime, calculated to be 184 nsec, due principally to Auger emission via the spin-dependent terms in the Breit interaction. This lifetime and the beam velocity of 7.6×10^7 cm/sec yield a decay length of 13.7 cm, which considerably exceeds the 4-cm length of the gas cell and accounts for the unshifted intensity seen in Figure 1-2(c).

The population of the $2p^5 3s 3p \ ^4D_{7/2}$ level could be taken as evidence for spin-reorientation in the two-electron-transfer collision; that is, one of the antiparallel electron

spins in the He target "flips" in the collision, producing the quartet ($S = 3/2$) projectile state. It is known, however, that this type of reorientation collision is improbable, and it is more likely that double capture occurs into states that are mixtures of $S = 1/2$ and $S = 3/2$, which subsequently radiatively decay to the metastable $^4D_{7/2}$ state.

Including the metastable $^4D_{7/2}$ state, a total of 17 spectral features have been measured and identified with calculated energies of $2p^5 3131'$ and $2p^5 3141'$ multiplets or individual levels in Fe^{15+} . The measured energies are in excellent agreement with the results of multiconfiguration Dirac-Fock calculations.

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2. Work in Progress: Alignment of Doubly Excited States

In any beam-gas inelastic collision, the final magnetic substates of the products are not necessarily equally populated. Because there is a preferred direction in the collision (the initial relative velocity vector), the system has cylindrical symmetry, and thus states with magnetic substate quantum numbers m_j and $-m_j$ will have equal population. Except for this restriction, the population of the different substates may differ. This variation of the magnetic substate population is called an alignment. For Auger states produced by electron-capture collisions, this alignment can result in a significant variation of the Auger line intensities with emission angle measured from the beam direction. Experiments using a large scattering chamber and a rotatable electron spectrometer are currently under way to measure the angular dependence of the Auger spectra following electron capture by several different highly charged ions from a gas-jet target. These will be the first systematic studies of Auger angular distributions from states created in slow, highly charged ion-atom collisions. Nearly all published Auger spectra have been taken at a single fixed angle with respect to the projectile beam. Measurement of the electron emission angular dependence allows inference of the underlying alignment and provides a detailed test of theoretical calculations of magnetic substate populations. It is also essential to know the angular dependence if one is to infer reliable cross sections from measurements made at fixed angles. The measurements will concentrate on well-characterized spectral features in the L-Auger spectrum of systems such as the well-studied $\text{O}^{6+} + \text{He}$ system. Strong emphasis will be placed on calibration of the instrument response by measuring lines known to produce isotropic distributions because of their quantum symmetry.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. R. Hutton, M.H. Prior, S. Chantrenne, M.H. Chen, and D. Schneider, "Double and Single Electron Capture in Slow Collisions of Ar^{9+} , $^{8+}$ Ions with He Atoms," *Phys. Rev. A* **39**, 4902 (1989); LBL-26581.
2. D. Schneider, M.H. Chen, S. Chantrenne, R. Hutton, and M.H. Prior, "Auger Electron Emission from Na-like Fe Ions Excited in Collisions of 170-keV Fe^{17+} on He and Ne," *Phys. Rev. A* **40**, 4313 (1989).
3. D.L. Weathers, T.A. Tombrello, M.H. Prior, R.G. Stokstad, and R.E. Tribble, "Sputtering of Au, CsI and LiNbO_3 by Multiply Charged Ar Ions," *Nucl. Instrum. Meth. Phys. Res. B* **42**, 307 (1989).
4. D.J. Clark, C.M. Lyneis, M.H. Prior, R.G. Stokstad, S. Chantrenne, and P.O. Egan, "The Atomic Physics Facility at the LBL ECR Source," *Nucl. Instrum. Meth. in Phys. Res. B* **40/41**, 6 (1989); LBL-25423.
5. J. Ullrich, R.E. Olson, H. Berg, S. Kelbch, R. Doerner, C. Kelbch, H. Schmidt-Boecking, S. Hagmann, P. Richard, M. Prior, and A.S. Schlachter, "Multiple Ionization and Collision Dynamics in High-Energy Uranium-Rare Gas Collisions," *Nucl. Instrum. Meth. Phys. Res. B* **40/41**, 149 (1989).

Other Publications

6. R. Hutton, M.H. Prior, D. Schneider, S. Chantrenne, and M.H. Chen, "Auger Spectra from Na-like Ions Produced in Si^{5+} , Ar^{9+} , Ti^{13+} , Fe^{17+} and Cu^{20+} + He Collisions," *Bull. Am. Phys. Soc.* **34**, 1358 (1989).
7. J.R. Alonso, D.D. Dietrich, M.H. Prior, and D.H.G. Schneider, Eds., *Proc. Workshop on Highly Charged Ions: New Physics and Advanced Techniques, Berkeley, March 13-15, 1989*, *Nucl. Instrum. Meth. Phys. Res. B* **43**, 265 (1989).
8. R. Herrmann, M. Prior, R. Doerner, H. Berg, H. Schmidt-Boecking, and C. Lyneis, "Multiple Electron Capture in Slow Collisions of Highly Charged Ne Ions on Ne," in *Abstracts Contrib. Papers XVI Int. Conf. Phys. Electronic and Atomic Collisions (ICPEAC)*, New York, NY, July 26-Aug. 1, 1989, A. Dalgarno *et al.*, Eds., p. 548.

9. J.A. Tanis, D. Schneider, M. Prior, S. Chantrenne, R. Herrmann, and R. Hutton, "Correlated Continuum- and Bound-State Capture in 60 keV O^{6+} + He Collisions," in *Abstracts Contrib. Papers XVI Int. Conf. Phys. Electronic and Atomic Collisions (ICPEAC)*, New York, NY, July 26-Aug. 1, 1989, A. Dalgarno *et al.*, Eds., p. 696.
10. D. Schneider, R. Bruch, M. Prior, and R. Hutton, "Li-like Auger States in Ne Following Slow (keV) and Fast (MeV) Ion Atom Collisions," in *Abstracts Contrib. Papers XVI Int. Conf. Phys. Electronic and Atomic Collisions (ICPEAC)*, New York, NY, July 26-Aug. 1, 1989, A. Dalgarno *et al.*, Eds., p. 605.
11. D. Schneider, R. Hutton, P. Beiersdorfer, M. Prior, S. Chantrenne, and M. Chen, "Comparison of Na-like Auger States Excited in MeV/u and keV/u Highly Charged Ti- and Ar-Ions," in *Abstracts Contrib. Papers XVI Int. Conf. Physics of Electronic and Atomic Collisions (ICPEAC)*, New York, NY, July 26-Aug. 1, 1989, A. Dalgarno *et al.*, Eds., p. 606.
12. R. Hutton, M.H. Prior, S. Chantrenne, M.H. Chen, and D. Schneider, "Isoelectronic Studies of Double and Single Electron Capture in Slow Ion-Atom Collisions," in *Abstracts Contrib. Papers XVI Int. Conf. Phys. Electronic and Atomic Collisions (ICPEAC)*, New York, NY, July 26-Aug. 1, 1989, A. Dalgarno *et al.*, Eds., p. 607.
13. R. Hutton, M.H. Prior, S. Chantrenne, M.H. Chen, and D. Schneider, "Electron Capture Studies for Slow, Heavy Ion Projectiles Colliding on He Atom Targets," in *Abstracts Contrib. Papers XVI Int. Conf. Phys. Electronic and Atomic Collisions (ICPEAC)*, New York, NY, July 26-Aug. 1, 1989, A. Dalgarno *et al.*, Eds., p. 608.
14. R. Hutton, M.H. Prior, S. Chantrenne, M.H. Chen, and D. Schneider, "Identification of the $2p^5 3s 3p^4 \text{D}_{7/2}$ Level in Na-like Ions Formed in Slow Ion-Atom Collisions," in *Abstracts Contrib. Papers XVI Int. Conf. Phys. Electronic and Atomic Collisions (ICPEAC)*, New York, NY, July 26-Aug. 1, 1989, A. Dalgarno *et al.*, Eds., p. 603.

Invited Talks

15. M.H. Prior, "Highly Charged Quasi-Molecules—Ion Atom Collision Studies at the LBL ECR Ion Source," Symposium of the Division of Nuclear Chemistry and Technology, American Chemical Society National Meeting, Dallas, TX, Apr. 9-14, 1989.

PROCESSES AND TECHNIQUES

CHEMICAL ENERGY

Formation of Oxyacids of Sulfur from SO_2^*

Robert E. Connick, Investigator

INTRODUCTION

The stimulus for this research is the existence of acid rain. Coal-burning power plants produce sulfur dioxide, which is oxidized in air to form sulfuric acid, the principal component of acid rain. In most commercial flue-gas desulfurization processes, the sulfur dioxide is absorbed in an aqueous solution of low acidity, where it may be oxidized by O_2 . Control of the rate of this latter reaction is of major importance to these processes. While recent research of the project has been concentrated on this reaction, investigation of the fundamental chemistry of species formed from sulfur dioxide and reactions of these species remains the primary goal. The oxidation-reduction chemistry of sulfur should be studied, particularly reactions between two oxidation states of the element, e.g., reactions involving HSO_3^- , H_2S , S_8 , and the polythionates. A secondary and not closely related goal is to determine the factors controlling the rate of substitution reactions in the first coordination sphere of metal ions in solution. Computer modeling has been extended to three dimensions, and configurations of activated complexes have been determined. The usual concept of a transition state with reflection coefficient near unity is quite inadequate.

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1. Work in Progress

Rate Law and Mechanism of the Oxidation of Bisulfite Ion by Oxygen

With the identification of monohydrogen peroxy monosulfate ion, HSO_5^- , as the intermediate in the reaction responsible for the formation of disulfate ion, $\text{S}_2\text{O}_7^{2-}$, attention has been focused on its chemistry. The kinetics of the reaction of HSO_5^- with HSO_3^- is under study. Because the reaction is very fast, it is studied at low concentrations of the reactants — between 10^{-4} and 2×10^{-6} M using the absorbance of HSO_3^- at 295 m μ . Results indicate a rate law of the form $[\text{HSO}_3^-][\text{HSO}_5^-][\text{H}^+]$ in the pH region 3.5 to 5 and a second term, important at higher pH, of the form $[\text{HSO}_3^-][\text{HSO}_5^-][\text{H}^+]^{-1}$. From a mechanistic point of view, it is interesting that the analogous two terms also appear in the rate law for the reaction between HSO_3^- and H_2O_2 . The accepted mechanism for the first term, by analogy, would lead to the formation of $\text{S}_2\text{O}_7^{2-}$ in the case of peroxy monosulfate. The next step will be to examine in detail the yield of $\text{S}_2\text{O}_7^{2-}$ in the reaction in order to understand the anomalies found earlier.

Modeling of Displacement Reactions of Solvent in the First Coordination Sphere of Metal Ions

Computer simulation of exchange of solvent from sixfold coordinated metal ions is continuing. Releases of the system constrained to be near the configuration of the activated complex have yielded results that depend on where the release is made. To alleviate this difficulty, releases are being made well to one side of the activated complex, but as a consequence many such releases are required to yield a single exchange event. The resulting pattern of activated complexes is not yet clear.

Potentially Catalytic and Conducting Polyorganometallics*

K. Peter C. Vollhardt, Investigator

INTRODUCTION

The task being carried out under this program is the synthesis and evaluation of new, multimetallic molecules designed to exhibit novel chemical behavior, particularly the catalysis of organic transformations of synthetic and industrial importance and potential conductivity. It centers on the development and execution of synthetic methodology aimed at allowing access to sequences of extended strong π -ligands to multiple transition metals. Although new work has as its target a variety of novel organic systems, most of the investigations so far have focused on the exploitation of a new, iterative strategy that allows the continued elaboration of linked cyclopentadienyl chains and their complexation with control of the resulting oligometallic sequence. In this way, a number of hitherto unknown transition metal arrays have become available in which the metallic centers adopt "unnatural" linear and angular configurations. These structures give rise to unprecedented reactivity when exposed to small molecules, pointing toward applications in catalysis. They also provide ideal models with which to probe the elementary steps of multimetallic ligand and electron transfer. The discovery of exciting preliminary chemistry of these systems, including thermally and photochemically induced intramolecular transfer of organic fragments, has justified the original premise of this research. Current efforts concentrate on exploring the reactivity patterns of the structures under investigation and expanding the range of available ligand chains.

1. Site-Specific Synthesis of Heterodinuclear Fulvalene Complexes (Publication 2)

A.P. Kahn, D.A. Newman, and K. P.C. Vollhardt

The study of heterodinuclear transition metal complexes has received considerable attention in the anticipation that the combination of the different properties of each metal center may give rise to unique or enhanced

reactivity patterns as compared to those found in simple homodinuclear systems. The fulvalene ligand is a particularly attractive matrix upon which to study metal-metal interactions, as it combines the thermodynamic and kinetic robustness offered by the cyclopentadienyl fragment with the possibility of electronic communication between the metal nuclei through the delocalized system of π -electrons.

It has been found that site selectivity in fulvalene metalation can be achieved when one cyclopentadienyl ring is masked in the form of a cyclopentenone, a substituent that is unreactive towards metalation but can be elaborated easily to the required cyclopentadiene. Introduction of the enone moiety was readily accomplished by a conjugate addition-elimination sequence involving 3-ethoxy-2-cyclopentenone and sodium cyclopentadienide (see Figure 1-1), providing the substituted cyclopentadienide **1**. Reaction of **1** with $W(CO)_3(MeCN)_3$ in THF, followed by the addition of MeI, resulted in tungsten-enone **2**. Conversion to the desired tungsten-diene **4** was accomplished by $LiAlH_4$ reduction to the enol **3**, followed by acid-catalyzed dehydration to produce **4**, as an inseparable mixture of 1,3- and 1,4-diene isomers. Addition of **4** to boiling solutions of the appropriate metal carbonyl reagent afforded the metal-metal bonded derivatives **5-8** in good yields (see Table 1-1). Alternatively, deprotonation of the cyclopentadiene functionality of **4** could be achieved with NaH, followed by metalation, using a variety of transition metal halides to produce **9-15** (see Table 1-1).

Figure 1-1. Conjugate addition-elimination sequence involving 3-ethoxy-2-cyclopentanone and sodium cyclopentadienide. (a) DME, reflux, 2 h; (b) $W(CO)_3(MeCN)_3$, THF, rt, 15 min; MeI, 10 min; (c) $LiAlH_4$, Et_2O , $0^\circ C$, 30 min; (d) cat. *p*-TsOH, C_6H_6 , $60^\circ C$, 3 min. (XBI. 903-886)

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Table 1-1. Synthesis of heterodinuclear fulvalenedimetals from compound **4**. (XBL 903-887)

The construction of **16** and **17** (see Table 1-1) was accomplished by the addition of **4** to a solution of the metal carbonyl reagent containing *tert*-butylethylene as a hydrogen acceptor.

The ready availability of cyclopentadienide **1** as a precursor to other analogues of type **2** provides a potentially general construction of fulvalene derivatives containing many combinations of transition metals.

2. The Photochemistry of (Fulvalene)diruthenium-(tetracarbonyl) and its Derivatives (Publication 8)

R. Boese,[†] W.B. Tolman, K.P.C. Vollhardt, and T.W. Weidman

Broadband irradiation ($\lambda_{\text{max}} = 350 \text{ nm}$) of a yellow THF solution of $\text{FvRu}_2(\text{CO})_4$ resulted in rapid isomerization to afford colorless $(\mu_2\text{-}\eta^1\text{:}\eta^5\text{-cyclopentadienyl})_2\text{Ru}_2(\text{CO})_4$. This compound reverted to its photoprecursor upon heating in solution or in the solid state, the latter being associated with an enthalpy change of $-29.8 (1.5) \text{ kcal mol}^{-1}$, as determined by differential scanning calorimetry. Prolonged irradiation of either complex with 300-nm light yielded decarbonylated products: the novel cluster $\text{Fv}(\mu_2\text{-}\eta^1\text{:}\eta^5\text{-cyclopentadienyl})_2\text{Ru}_4(\text{CO})_6$, in the absence of added ligands, or adducts $\text{FvRu}_2(\text{CO})_3(\text{RCCR})$ ($\text{R} = \text{H, Ph, CO}_2\text{Me}$), in the presence of alkynes. X-ray crystal analyses of the first four complexes were carried out. Treatment of $\text{FvRu}_2(\text{CO})_4$ with PR_3 ($\text{R} = \text{CH}_2\text{CH}_3, \text{CH}_3$, and OCH_3) yielded the monosubstituted derivatives $\text{FvRu}_2(\text{CO})_3(\text{PR}_3)$, the ^1H and ^{13}C NMR spectra of which indicated the occurrence of a fluxional process in solution involving intramolecular terminal-to-bridging-carbonyl exchange. While the trialkylphosphine-substituted species remained unchanged on irradiation, the phosphite derivative ($\text{R} = \text{OCH}_3$) rapidly and reversibly afforded the $\text{P}(\text{OCH}_3)_3$ -substituted photoisomer on exposure to UV light. A crossover experiment employing $d_8\text{-FvRu}_2(\text{CO})_4$ showed that both the photochemical and thermal rearrangements are intramolecular. The average quantum yield for the former was determined to be 0.15 (3), a value that appeared independent of the nature of the reaction media. Experiments using 3,3'-di-*tert*-butyl-substituted Fv complexes ruled out the occurrence of inversion and/or randomization of stereochemistry with respect to the cyclopentadienyl rings during the photoreaction or its thermal reverse. Thus, treatment of 3,3'-di-*tert*-butylfulvalene with $\text{Ru}_3(\text{CO})_{12}$ afforded the diastereomers (S^*, S^* - and S^*, R^* -3, 3'-di-*tert*-butylfulvalene) $\text{Ru}_2(\text{CO})_4$, which upon UV irradiation stereospecifically and reversibly transformed to different stereoisomers. Double regiochemical labeling experiments were performed, employing derivatives in which the two Cp rings of the Fv

were differentiated by the introduction of a single *tert*-butyl group, the two metals by single $\text{P}(\text{OCH}_3)_3$ substitution, synthesized by treatment of (3-*tert*-butylfulvalene) $\text{Ru}_2(\text{CO})_4$ with $\text{P}(\text{OCH}_3)_3$. Distinctly regioisomeric photoisomers were generated with retention of connectivity, one of which was structurally characterized by x-ray crystallography, the others by NMR methods. Solution kinetic data on the thermal reversal of several of the photoproducts to their respective metal-metal bonded precursors were collected between 65 and 99°C in diglyme or decane, exhibiting remarkably little variation in magnitude. [For the parent, $\Delta H^\ddagger = 29.9$ (9) kcal mol⁻¹ and $\Delta S^\ddagger = +17$ (2) eu.] The combined data argue for a concerted isomerization pathway.

[†]Permanent address: Institute of Inorganic Chemistry, University-GH Essen, D-4300 Essen 1, Federal Republic of Germany.

3. Tandem Palladium-, Cobalt-, and Nickel-Catalyzed Syntheses of Polycyclic π -Systems Containing Cyclobutadiene, Benzene, and Cyclooctatetraene Rings (Publication 6)

H. Schwager,[†] S. Spyroudis,[‡] and K.P.C. Vollhardt

A (potentially iterative) reaction sequence has been developed that exploits the specific catalytic activity of certain palladium, cobalt, and nickel complexes in succession to provide a simple and efficient access to novel polycyclic π -electron systems. It begins with a suitable 1,2-dihaloarene and its Pd^{2+} -catalyzed diethynylation, continues (after alkyne deprotection) with the cyclopentadienylcobalt-catalyzed alkyne co-cyclization of the product to give the biphenylene nucleus, and ends with the Ni^0 -catalyzed dimerization of the latter to furnish derivatives of tetrabenzocyclooctatetraene (see Figure 3-1). The methodology should have an impact on a number of research efforts, including (1) the possible use of biphenylene-based monomers for the preparation of novel, potentially conducting polymers or, along related lines, such treatment of biphenylene-bearing polymers to undergo crosslinking to similar materials; (2) the construction of novel structures of theoretical or bioorganic importance; (3) a more general access to substituted tetrabenzocyclooctatetraenes, recently shown to exhibit interesting properties; and (4) the tailored assembly of extended multidentate π -ligands to transition metals.

[†]Recipient of an Otto-Hahn and a Max-Planck Institute for Coal Research (Mulheim) fellowship (1986–1987).

[‡]Sabbatical leave fellowship (1986–1987) from the University of Thessaloniki, Greece.

Figure 3-1. Reaction sequence that leads to novel polycyclic π -electron systems. (a) $\text{Me}_3\text{SiC}\equiv\text{CH}$, Et_3N , $\text{PdCl}_2(\text{PPh}_3)_2$; (b) KOH , MeOH ; (c) $\text{RC}\equiv\text{CR}$, $\text{CpCo}(\text{CO})_2$, $h\nu$; (d) $\text{Ni}(\text{COD})(\text{PMe}_3)_2$. (XBL 903-888)

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. J.A. King, Jr., and K.P.C. Vollhardt, "The Thermal and Photochemical Degenerate 'Walk' of (η^5 -Cyclopentadienyl)cobalt Along η^4 -Bound 1,3,5-Hexatriene," *J. Organomet. Chem.* **369**, 245 (1989); LBL-26644.
2. A.P. Kahn, D.A. Newman, and K.P.C. Vollhardt, "Site-Specific Synthesis of Heterodinuclear Fulvalene Complexes," *Synlett.*, 119 (1990); LBL-28425.

LBL Reports

3. I. Amer, T. Bernstein, M. Eisen, J. Blum, and K.P.C. Vollhardt, "Oligomerization of Alkynes by the RhCl_3 -Aliquat 336 Catalyst System. Part 1. Formation of Benzene Derivatives," LBL-28420.
4. M.C. Kerby, B.W. Eichhorn, and K.P.C. Vollhardt, "Activated Mo-Mo Quadruple Bonds. 2. The First Example of Alkyne Addition to a Metal-Metal Quadruple Bond," LBL-28421.
5. S.J. Potlock, J.S. Merola, R. Liotta, T.R. Halbert, and K.P.C. Vollhardt, "Carbon-Carbon Bond Activation in Hexakis(trifluoromethyl)benzene: Effect of Ancillary Ligands (L) in Pt^0L_2 Reactions," LBL-28422.
6. H. Schwager, S. Spyroudis, and K.P.C. Vollhardt, "Tandem Palladium-, Cobalt- and Nickel-catalyzed Syntheses of Polycyclic π -Systems Containing Cyclobutadiene, Benzene and Cyclooctatetraene Rings," *J. Organomet. Chem.* (in press); LBL-28423.
7. I. Amer, J. Blum, and K.P.C. Vollhardt, "Oligomerization of Alkynes by the RhCl_3 -Aliquat 336 Catalyst System. Part 2. Formation of 2,3-Disubstituted 1-Phenylnaphthalenes by Cyclodimerization of Phenylalkynes," LBL-28424.

8. R. Boese, W.B. Tolman, K.P.C. Vollhardt, and T.W. Weidman, "The Photochemistry of (Fulvalene)diruthenium(tetracarbonyl) and Its Derivatives," LBL-28552.

Invited Talks

9. K.P.C. Vollhardt, "Oligocyclopentadienylmetals: Remarkable Organometallic Materials," *Frontiers in Chemistry* Lecturer, Case Western Reserve University, Cleveland, OH, Mar. 23, 1989; University of Santiago de Compostela, Spain, July 14, 1989; Boston University, Boston, MA, Oct. 16, 1989.
10. K.P.C. Vollhardt, "Transition-metal Mediated Total Synthesis of Natural and Unnatural Products," plenary lecturer, *Symposium on Frontiers in Chemistry, AAAS Annual Meeting*, San Francisco, CA, Jan. 14-19, 1989; New Mexico State University, Albuquerque, NM, Jan. 26, 1989; University of Texas, El Paso, Jan. 27, 1989; University of Southern California, Los Angeles, Feb. 22, 1989; plenary lecturer, 8th Biennial Carl S. Marvel Symposium, University of Arizona, Tucson, Mar. 13-14, 1989; Purdue University, Lafayette, IN, Mar. 21, 1989; *Frontiers in Chemistry* Lecturer, Case Western Reserve University, Cleveland, OH, Mar. 23, 1989; University of California at Irvine, Sept. 28, 1989; Parke-Davis, Ann Arbor, MI, Oct. 12, 1989; Catalytica Associates, Menlo Park, CA, Oct. 25, 1989.
11. K.P.C. Vollhardt, "Trialkylsilyl Substituent Control of Chemo-, Regio-, and Stereoselectivity in Cobalt-Mediated Total Syntheses of Natural and Unnatural Products," plenary lecturer, 22nd Organosilicon Symposium, Bristol, PA, Apr. 7-8, 1989.
12. K.P.C. Vollhardt, "An Introduction to Organometallic Chemistry," minicourse (five lectures), University of Santiago de Compostela, Spain, July 10-14, 1989.
13. K.P.C. Vollhardt, "Organic Transformations Involving Organocobalt: Mechanisms and Synthesis," plenary lecturer, *Symposium on Organic Transformations Involving Organometallics: Mechanism and Synthesis*, 1989 International Chemical Congress of Pacific Basin Societies, Honolulu, HI, Dec. 17-22, 1989.

High-Energy Oxidizers and Delocalized-Electron Solids*

Neil Bartlett, Investigator

INTRODUCTION

The main aim of this program is the synthesis and characterization of new materials that may have utility in efficient storage or usage of energy. The novel materials include two-dimensional networks of light π -bonding atoms (boron, carbon, and nitrogen) with structures akin to graphite. Of these, the more metallic have possible applications as electrode materials for high-energy-density batteries, and those that are semiconducting could be useful in converting light to electrical energy. Good ionic conductors are also being sought, with emphasis on lithium-ion and fluoride-ion conductors, since batteries based on lithium and fluorine would be unsurpassed in their energy-density features. In addition, novel-oxidation-state fluorides are being synthesized and structurally characterized to provide a comprehensive basis for better theoretical models, from which an improved capability to predict physical and chemical behavior ought to be forthcoming. Previously unknown or little-studied high-oxidation-state species constitute a large part of this effort. Such species are also investigated for their efficiency and specificity as chemical reagents.

1. The Spontaneous Oxidation of Xenon to Xe(II) by Cationic Ag(II) in Fluoroacid Solutions (Publication 6)

B. Žemva,[†] R. Hagiwara, W.J. Casteel, Jr., K. Lutar,[†] A. Jesih,[†] and N. Bartlett

Blue solutions of AgF_2 , dissolved in anhydrous hydrogen fluoride (AHF) by the addition of fluoride-ion acceptors (mono-acids) such as BF_3 or AsF_5 , rapidly oxidize xenon at $\sim 20^\circ\text{C}$ to give colorless solutions of XeF_2 , or its salts, and precipitate colorless Ag(I) salts (AgBF_4 or AgAsF_6). Overall reactions (AHF removed) are:

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AgF_2 in the absence of fluoride-ion acceptors does not oxidize Xe under comparable conditions; hence the potent oxidizing power is probably associated with HF-solvated cationic species such as $(\text{AgF})^+$ or Ag^{2+} . A μ -fluoro-bridged polymeric version of the former has been described¹ in the salt $\text{AgF}^+\text{AsF}_6^-$, and the latter is seen² in $\text{Ag}^{2+}(\text{SbF}_6)_2$, where the cation exhibits elongated octahedral coordination, consistent with a Jahn-Teller distortion associated with the d^9 electron configuration of Ag^{2+} . AgF_2 with BF_3 in AHF yields the blue solid AgFBF_4 , which is tetragonal, with $a_0 = 6.70(1) \text{ \AA}$ and $c_0 = 4.01(1) \text{ \AA}$; $V = 180 \text{ \AA}^3$; $z = 2$. The structure is probably related to that of the AgFAsF_6 salt, in which case the polymeric cation chain must run parallel to c_0 . It is possible that solvated AgF^+ is the solution species that oxidizes Xe, but excess acid increases the rate of oxidation, and this could signify that the effective oxidizer is, rather, solvated Ag^{2+} . No matter what the coordination geometry of Ag^{2+} , the d^9 electron configuration must exert strong antibonding character (both sigma and pi) towards any donor ligand such as F (which also has $p\pi$ donor character). Bonding of fluorine to Ag^{2+} must therefore be weak, and its solvation energy may not be much greater than that for Xe atom. The electron affinity (eV) of $\text{Ag}_{(g)}^{2+}$ (21.49) is the highest of the common metal dications and, perhaps significantly, exceeds that of $\text{Xe}_{(g)}^{2+}$ (21.21). The interaction of cationic Ag(II) in AHF with Xe may, therefore, involve electron transfer from Xe to cationic Ag(II) as the first step in this remarkable reaction.

Since Ag(I) is oxidized by F_2 in acidic AHF to cationic Ag(II), it catalyzes the interaction of Xe with F_2 ($\text{Xe} + \text{F}_2 \rightarrow \text{XeF}_2$), but XeF_2 competes effectively as a fluorobase with AgF_2 in AHF and displaces it from solution ($\text{AgF}^+ + 2\text{XeF}_2 \rightarrow \text{Xe}_2\text{F}_3^+ + \text{AgF}_2$). To maintain the Ag(I/II) catalyst and the acidity essential to the oxidation of Xe by the Ag(II), the XeF_2 fluorobase that is formed must be neutralized with acid, e.g., $2\text{Xe} + 2\text{F}_2 + \text{AsF}_5 \rightarrow \text{Xe}_2\text{F}_3\text{AsF}_6$.

[†]Permanent address: Institute Jozef Stefan, Ljubljana, Yugoslavia.

1. D. Gantar, B. Frljč, D.R. Russell, and J.H. Holloway, *Acta Crystallogr. C* **43**, 618 (1987).

2. D. Gantar, I. Leban, B. Frljč, and J.H. Holloway, *J. Chem. Soc., Dalton Trans.*, 2379 (1987).

2. The Preparation, Structure, and Some Chemistry of Silver Trifluoride (Publication 7)

B. Žemva,[†] K. Lutar,[†] J. Jesih,[†] A.P. Wilkinson, D.E. Cox,[†] W.J. Casteel, Jr., and N. Bartlett

Solutions of AgF_4^- salts in AHF, at 20°C or below, yield a bright red precipitate of AgF_3 , with strong F^- acceptors (fluoroacids)¹ such as BF_3 and AsF_5 (e.g., AgF_4^-

+ BF₃ → AgF₃ + BF₄⁻). With the strong acid AsF₅, it is essential to avoid a local excess of acid in the preparation, since AgF₃ interacts with that excess, in AHF, to form the Ag(II) salt, AgFAsF₆, with liberation of F₂ (AgF₃ + AsF₅ → 1/2 F₂ + AgFAsF₆). Precipitation with BF₃ avoids that difficulty. Stoichiometric AgF₃ is indefinitely stable at room temperature in sealed fluoro-ethylene polymer (FEP) tubes and attacks dry quartz only slowly; but if slight fluorine loss has occurred because of local excess of acid in the preparation, the fluoride transforms to a brown paramagnetic solid of different and unknown structural form, identical with a material previously claimed² to be AgF₃. Stoichiometric AgF₃ is isostructural with AuF₃ and is diamagnetic (i.e., low-spin d⁸). A refinement of the AgF₃ structure carried out using 1.24805-Å wavelength x rays of the Brookhaven National Laboratory Synchrotron Facility has yielded a precise structure. The refinement rapidly converged to R_{wp} = 5.3% and R_f = 4.7%, in space group P6₁22-D₆². The hexagonal unit cell has a₀ = 5.0753(3) Å and c₀ = 15.448(1) Å; V = 344.58 Å³; z = 6. The formula unit volume (57.43 Å³) is ~5 Å³ less than that of its gold relative,³ even though the unit cell of metallic gold is slightly smaller than that of silver. These size changes are in accord with relativistic effects associated with s orbital electrons, which are particularly large for gold. The comparison of the elongated octahedral coordination in AgF₃ and AuF₃ is brought out in Figure 2-1, where long-bonded Ag-F = 2.53(1) Å and Au-F = 2.69(4) Å. This points to tighter binding of the d_z² electron pair in Ag(III) compared with Au(III) and is in harmony with the chemistry. All efforts to oxidize Ag(III) fluorospecies have

Figure 2-1. The coordination geometry about the Ag(III) atom in AgF₃. (XBL 903-889)

failed, whereas Au(III) fluorospecies are readily converted⁴ to Au(V) relatives.

Stoichiometric AgF₃ interacts with Xe at ~20°C according to the equation

AHF solutions of AgF₄⁻ are also reduced by Xe:

but in the presence of fluoroacid the Ag(III) is reduced to Ag(I):

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[‡]Permanent address: Brookhaven National Laboratory, Upton, NY 11973.

1. B. Žemva, K. Lutar, A. Jesih, W.J. Casteel, Jr., and N. Bartlett, J. Chem. Soc., Chem. Commun., 346 (1989).

2. R. Bougon and M. Lance, C.R. Seances Acad. Sci., Ser. 2, 297, 117 (1983).

3. F.W.B. Einstein, P.R. Rao, J. Trotter, and N. Bartlett, J. Chem. Soc., A, 478 (1967).

4. K. Leary and N. Bartlett, J. Chem. Soc., Chem. Commun., 903 (1972).

3. Crystal Structures of XeF₅⁺MF₄⁻ (M = Ag, Au) and their Relevance to the Basicity and Oxidizability of MF₄⁻ (Publication 3)

K. Lutar,[†] A. Jesih,[†] I. Leban,[†] B. Žemva,[†] and N. Bartlett

XeF₅⁺AuF₄⁻ has been prepared from BrF₃AuF₃ by displacement of BrF₃ with XeF₆. The salt interacts quantitatively with KrF₂ in anhydrous HF, below 0°, to yield XeF₅⁺AuF₆⁻. XeF₅AuF₄(I) is isostructural with XeF₅AgF₄(II), which crystallizes in space group I4/m with unit cell dimensions (I) a₀ 5.735(5) Å, c₀ = 20.007(17) Å, V = 658(2) Å³, z = 4; and (II) a₀ = 5.593(2) Å, c₀ = 20.379(5) Å, V = 637.5(8) Å³, z = 4. The structure of (II) was solved by the Patterson method and refined to conventional R and R_w values of 0.077 and 0.090, respectively. The structure contains double layers of XeF₅⁺ and layers of AgF₄⁻ ions, all layers being parallel to the *ab* plane. The XeF₅⁺ has C_{4v} symmetry, with Xe-F axial = 1.853(19) Å and Xe-F equatorial = 1.826(9) Å, and F axial-Xe-F equatorial = 77.7(3)°. The anion (site symmetry D_{2h}), which is not significantly different from D_{4h} symmetry, has Ag-F = 1.902(11) Å. The AgF₄⁻ is ~5 Å³ smaller in effective volume than AuF₄⁻. This suggests that the effective nuclear charge at Ag(III) is larger than that at Au(III). If so, the F ligand charge in AuF₄⁻ would be larger

than in its silver analogue. This is consistent with the shorter c_0 dimension in the AuF_4^- salt, which probably represents a stronger interaction between the cation and anion layers. The relatively easy oxidation of AuF_4^- ($\text{AuF}_4^- + \text{KrF}_2$, in AHF at $<0^\circ\text{C}$, $\rightarrow \text{AuF}_6 + \text{Kr}$), and the failure to similarly oxidize AgF_4^- , also testify to the tighter binding of the d_z^2 valence-electron pair in Ag(III) than in Au(III) .

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4. Work in Progress

A B/C/N graphite richer in B and N than BC_2N can be prepared at $\sim 700^\circ\text{C}$ by interaction of CH_3NCl [prepared from CH_3NH_2 and $\text{C}_2\text{H}_4(\text{CO})_2\text{NCl}$] with BCl_3 . It and other B/C, C/N, and B/C/N, materials are being characterized both physically and chemically. Intercalation by lithium metal or by the oxidizer $\text{S}_2\text{O}_6\text{F}_2$ appears to be possible for all of these materials.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. B. Žemva, K. Lutar, A. Jesih, W.J. Casteel, Jr., and N. Bartlett, "A General Method for the Synthesis of Polymeric Binary Fluorides Exemplified by AgF_3 , NiF_4 , RuF_4 , and OsF_4 ," *J. Chem. Soc., Chem. Commun.*, 346 (1989); LBL-25805.
2. R. Hagiwara, M. Lerner, and N. Bartlett, "The Preparation of Planar-sheet Graphite Fluorides C_xF with $x < 2$," *J. Chem. Soc., Chem. Commun.*, 573 (1989); LBL-25794.
3. K. Lutar, A. Jesih, I. Leban, B. Žemva, and N. Bartlett, "The Crystal Structures of XeF_5MF_4 ($M = \text{Ag}$ and Au) and their Relevance to the Basicity and Oxidizability of MF_4 ," *Inorg. Chem.* **28**, 3467 (1989); LBL-25395.

Other Publications

4. N. Bartlett, "Valency in the Periodic Table—Concerning the Limits of Oxidation of the Elements," *The Robert A. Welch Foundation Conference, Chapter X, XXXII Valency*, 1988, p. 259.

LBL Reports

5. N. Bartlett, F. Okino, T.E. Mallouk, R. Hagiwara, M. Lerner, G. Rosenthal, and K. Kourtakis, "Evidence that the Barrier to Oxidative Intercalation of Graphite by Fluoroanionic Species is Thermodynamic," in *Advances in Chemistry series* (in press); LBL-28564.
6. B. Žemva, R. Hagiwara, W.J. Casteel, Jr., K. Lutar, A. Jesih, and N. Bartlett, "The Spontaneous Oxidation of

Xenon to Xe(II) by Cationic Ag(II) in Anhydrous Hydrogen Fluoride Solutions," LBL-28299.

7. B. Žemva, K. Lutar, A. Jesih, A.P. Wilkinson, D.E. Cox, W.J. Casteel, Jr., and N. Bartlett, "The Preparation, Structure and Some Chemistry of Silver Trifluoride," LBL-28565.

Invited Talks

8. N. Bartlett, "Novel Fluoro Graphites and Novel B/C, C/N, and B/C/N Graphites," University of Washington, Seattle, Jan. 10, 1989.
9. N. Bartlett, "Novel Graphite-Network Materials," AAAS Frontiers in Chemistry Symposium, San Francisco, CA, Jan. 17, 1989.
10. N. Bartlett, "The Role of Fluoroacidity, Electron Affinity, and Dielectric Spacer Effects in the Intercalation of Graphite by Fluorometallate Species," ACS Ninth Winter Fluorine Conference, St. Petersburg, FL, Feb. 2, 1989.
11. N. Bartlett, "New Graphite Related Materials," College of Engineering, Department of Materials Science and Mineral Engineering, University of California at Berkeley, Feb. 9, 1989.
12. N. Bartlett, "The Role of Lattice Energetics and the Electron Affinity of the Oxidizing-Reagent Combination in the Oxidative Intercalation of Graphite," ACS Biennial Inorganic Symposium, University of Georgia, Athens, Mar. 3, 1989.
13. N. Bartlett, "Novel Graphite Materials," Solid-State Physics Seminar, University of California at Berkeley, Mar. 15, 1989.
14. N. Bartlett, "Concerning the Synthesis of High-Oxidation-State Species," ACS Award Address, Dallas, TX, Apr. 10, 1989.
15. N. Bartlett, "Novel Aspects of Graphite Intercalation by Fluorine and Fluorides and new B/C, C/N, and B/C/N Materials Based on the Graphite Network," Freie Universität Berlin, Germany, May 22, 1989.
16. N. Bartlett, "Fluorine Chemistry of High Oxidation States," Graduate College on the Synthesis and Structure of Lower Molecular Weight Compounds, Technische Universität Berlin and Freie Universität Berlin, Germany, May 26, 1989.
17. N. Bartlett, "Nobel Gas Chemistry," Freie Universität Berlin, Germany, June 2, 1989.
18. N. Bartlett, "Chemistry of Graphites," Münster Section, Gesellschaft Deutscher Chemiker, Münster, Federal Republic of Germany, June 5, 1989.
19. N. Bartlett, "New Materials Based on Graphite-like Networks," Justus V. Liebig University, Giessen, Federal Republic of Germany, June 5, 1989.
20. N. Bartlett, "From Nobel-Gas Chemistry to Graphite Chemistry," Gesellschaft Deutscher Chemiker, Bremen, Federal Republic of Germany, June 6, 1989.
21. N. Bartlett, "The Synthesis and Properties of Novel Materials based on Graphite-like Networks," Stuttgart Section, Gesellschaft Deutscher Chemiker, Stuttgart, Federal Republic of Germany, June 19, 1989.

22. N. Bartlett, "New Aspects of Graphite Intercalation and Novel Materials having Graphite-like Structures," Nineteenth Biennial Conference on Carbon, Pennsylvania State University, University Park, June 28, 1989.
23. N. Bartlett, "Novel Aspects of Graphite Intercalation by Fluorine and Fluorides and New B/C, C/N, and B/C/N Materials Based on the Graphite Network," 40th Meeting, International Society of Electrochemistry, Kyoto, Japan, Sept. 18, 1989; Division of Molecular Engineering Seminar, Institute for Fundamental Chemistry, Kyoto University, Kyoto, Japan,
24. N. Bartlett, "Nobel-Gas Chemistry," Reed College, Portland, OR, Nov. 10, 1989.
25. N. Bartlett, "Assessing the Highest Oxidation States Attainable for The Elements," Pauling Medal Symposium, Portland State University, Portland, OR, Nov. 11, 1989.

Transition Metal-Catalyzed Conversion of CO, NO, H₂, and Organic Molecules to Fuels and Petrochemicals*

Robert G. Bergman, Investigator

INTRODUCTION

The goal of this program is the development of new chemical reactions in which transition metals interact with organic materials, and the understanding of how these reactions work. A recent discovery on this project was the finding that certain metal complexes undergo oxidative addition into the carbon-hydrogen bonds of completely saturated hydrocarbons ($M + R-H \rightarrow R-M-H$). This finding was the first example of a long-sought "alkane C-H activation" reaction; research is now being directed at examining the scope, selectivity, and mechanism of the process, extending it to other X-H bonds, and developing ways to convert the activated metal complexes X-M-H into functionalized organic molecules. During the current year, progress was made on the activation of molecules containing the heteroatoms oxygen and nitrogen, such as epoxides, alcohols, and amines. Most significant, however, was the finding that the liquified noble gases krypton and xenon could be used as inert solvents for C-H activation reactions. This technique now permits reaction of iridium

and rhodium with C-H bonds in organic solids and very low boiling liquids (e.g., methane). It has also provided the first measurement of the fast rates and low activation energies of the direct C-H oxidative addition of rhodium to alkane C-H bonds.

1. Conversion of Epoxides to Rhodium Enolates: Direct Evidence for a Mechanism Involving Initial C-H Activation (Publication 1)

J. Wu and R.G. Bergman

Irradiation of $Cp^*(L)RhH_2$ [$Cp^* = (\eta^5-C_5Me_5)$; $L = PMe_3$; compound **1** in Figure 1-1)] for 3 hr in ethylene oxide (**2a**) solvent in a sealed nuclear magnetic resonance (NMR) tube held at temperatures below $-60^\circ C$ gives diastereomeric metallated epoxides $Cp^*(L)Rh(H)(CHCH_2O)$, **3a**, in over 95% NMR yield. Warming the tube slowly to $0^\circ C$ induces the rearrangement of **3a** to the carbon-bound metal enolate $Cp^*(Me_3P)Rh(H)(CH_2CHO)$, **4a**. Addition of CHI_3 to a solution of **3a** at $-78^\circ C$ results in replacement of the hydride ligand by iodide, giving $Cp^*(Me_3P)Rh(I)(CHCH_2O)$ (**5a**). The chemistry of **3a** and **5a** are analogous: at room temperature, **5a** rearranges to the iodo(iridium) enolate $Cp^*(Me_3P)Rh(I)(CH_2CHO)$ (**6a**; 81% yield by NMR). This complex has been characterized by x-ray diffraction, which revealed a substantially disordered

Figure 1-1. Transformations observed during the low-temperature C-H activation of ethylene oxide by rhodium, and an ORTEP diagram illustrating the x-ray structure of complex **6a** ($Cp^* = \eta^5-C_5Me_5$; $L = PMe_3$). (XBL 902-492)

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structure [structural data for **6a**: space group: *Pbca*; *a* = 16.0047(21) Å, *b* = 12.7997(16) Å, *c* = 18.0965(23) Å, *R* = 3.99%, *R_w* = 6.03%, GOF = 2.87]. An ORTEP diagram of the structure is included in Figure 1-1. Treatment of hydride rearrangement product **4a** with CHI₃ also leads to **6a**, identical with material obtained in the rearrangement of **5a**. These experiments demonstrate that C-H insertion product **3a** is an obligatory intermediate in the conversion of dihydride **1** and ethylene oxide to hydrido(enolate) **4a**. Thus the conventional metal-induced epoxide rearrangement mechanism involving initial attack of Rh on the small-ring C-O bond (to give either a ring-opened zwitterion or a four-membered oxametallacycle) cannot operate in this case. Isotope-labeling experiments using ethylene oxide-1,1-d₂, along with kinetics and solvent-effect studies, provide evidence that the rearrangement of metallated epoxide to rhodium enolate involves a 1,2-shift of hydrogen rather than rhodium.

2. Synthesis of a Highly Reactive (Benzyne)Ruthenium Complex: C-C, C-H, N-H, and O-H Activation Reactions (Publication 2)

J.F. Hartwig, R.A. Andersen, and R.G. Bergman

The new benzyne complex (PMe₃)₄Ru(η²-C₆H₄) (complex **1** illustrated in Figure 2-1) has been found to be the product of thermolysis of either Ru(Ph)₂(PMe₃)₄ or Ru(Ph)(Me)(PMe₃)₄. Kinetic evidence indicates that this thermolysis proceeds by a mechanism that involves initial dissociation of a phosphine ligand, followed by oxidative addition of a phenyl C-H bond to the metal center, as is typical for low-valent electron-rich compounds. However, much of the reactivity of **1** (summarized in Figure 2-1) is similar to that seen earlier in electrophilic, rather than electron-rich, benzyne complexes, and some is completely unprecedented. For example, complex **1** reacts

Figure 2-1. ORTEP diagram illustrating the x-ray structure of ruthenium benzyne complex **1**, and a summary of the synthesis and chemistry of this material (L = PMe₃). (XBL 902-493)

with the C-H bonds of hydrocarbons to undergo ring-exchange processes, and it reacts with OH and NH bonds to form monomeric hydroxide and amide complexes. Reaction of the benzyne complex with benzaldehyde yields simple M-C insertion products, while reaction with acetophenone yields an oxygen-bound enolate complex. The reaction of **1** with acetone is most unusual, cleaving the C-C bond of the organic substrate to yield methane, along with the same oxygen-bound enolate complex formed in the reaction with acetophenone.

3. Liquid Xenon: An Effective Inert Solvent for C-H Oxidative Addition Reactions (Publication 3)

M.B. Sponsler, B.H. Weiller, P.O. Stoutland, and R.G. Bergman

Liquid xenon has been used successfully as an inert solvent in photochemical C-H activation reactions of $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$ (**1**, $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$). As shown in Figure 3-1, irradiation of xenon solutions of **1** and hydrocarbons (RH) in the temperature range from -75 to -60°C provides the iridium alkyl hydride complexes, $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{H})(\text{R})$. The inert solvent has allowed the photochemical activation of several new substrates, such as methane, adamantane, cubane, and naphthalene. The use of alcohols as substrates results in insertion into either C-H or O-H bonds, depending on the alcohol. Thus, the use of methanol or ethanol as substrate in xenon yields the corresponding alkoxy hydride product. This result contrasts with the photochemistry observed in alcohol solvent, where products derived from C-H insertion are obtained.

Figure 3-1. Products formed on irradiation of solutions of **1** and the indicated organic molecules in liquid xenon at -60 to -75°C . (XBL 902-494)

4. Time-Resolved Infrared Spectroscopy in Liquid Rare Gases: Direct Rate Measurement of an Intermolecular Alkane C-H Oxidative Addition Reaction (Publication 4)

B.H. Weiller, E.P. Wasserman, R.G. Bergman, C.B. Moore, and G.C. Pimentel

The rate of oxidative addition of cyclohexane to form $\text{Cp}^*\text{Rh}(\text{CO})(\text{C}_6\text{H}_{11})(\text{H})$ [$\text{Cp}^* = (\eta^5\text{-C}_5\text{Me}_5)$] has been measured in liquid krypton over a wide range of temperatures and cyclohexane concentrations using a novel combination of low-temperature and infrared laser flash kinetic techniques. Photolysis of $\text{Cp}^*\text{Rh}(\text{CO})_2$ in liquid xenon produces a monocarbonyl species that is much less reactive than the one generated in liquid krypton. In the presence of C_6H_{12} , the monocarbonyl decays exponentially to form $\text{Cp}^*\text{Rh}(\text{CO})(\text{C}_6\text{H}_{11})(\text{H})$. As shown in Figure 4-1, the observed rate constant k_{obs} increases monotonically with increasing cyclohexane concentration and approaches an asymptotic value. When C_6D_{12} is used in place of C_6H_{12} , a significant isotope effect on the asymptotic rate constant is observed. A mechanism that accounts for these data consists of a rapid exchange equilibrium between the krypton complex, $\text{Cp}^*\text{Rh}(\text{CO})(\text{Kr})$, and an alkane complex, $\text{Cp}^*\text{Rh}(\text{CO})(\text{C}_6\text{H}_{12})$, followed by unimolecular insertion to form the alkyl hydride product. From the temperature dependence of the observed rate constants, activation

Figure 4-1. The observed rate constants (k_{obs}) for the decay of the rhodium monocarbonyl transient at 1947 cm^{-1} (filled symbols) formed on irradiation of $(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})_2$ in liquid Kr, and for the formation of the product $(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})(\text{C}_6\text{H}_{11})(\text{H})$ (2003 cm^{-1} , open symbols) as a function of cyclohexane concentration and temperature. For clarity, only representative error bars are indicated explicitly. (XBL 902-495)

parameters for the insertion reaction ($E_a = 4.8 \pm 0.2$ kcal/mol, $\log(A) = 11.2 \pm 0.2$) are derived.

5. Work in Progress

Research is currently under way on the following problems in C-H activation chemistry: (1) synthesis of metal complexes containing non-Cp-containing ligands (such as indenyl and dimethylphosphinoethane) to examine their C-H activation chemistry and utilize them to develop methods for converting C-H activation products to functionalized organic compounds; (2) extension of the use of liquified noble gases such as xenon and krypton as inert solvents for C-H activation studies with metals other than rhodium (e.g., iridium, rhenium) to determine direct activation energies for C-H activation in these solvents and compare them with values recently measured for rhodium; and (3) development of methods for detecting and studying alkane complexes of C-H activating metals, to determine the roles such complexes play in the C-H oxidative addition process.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. J. Wu and R.G. Bergman, "Conversion of Epoxides to Rhodium Enolates: Direct Evidence for a Mechanism Involving Initial C-H Activation," *J. Am. Chem. Soc.* **111**, 7628 (1989); LBL-28050.
2. J.F. Hartwig, R.A. Andersen, and R.G. Bergman, "Synthesis of a Highly Reactive (Benzynes)ruthenium Complex: C-C, C-H, N-H, and O-H Activation Reactions," *J. Am. Chem. Soc.* **111**, 2717 (1989); LBL-26480.
3. M.B. Sponsler, B.H. Weiller, P.O. Stoutland, and R.G. Bergman, "Liquid Xenon: An Effective Inert Solvent for C-H Oxidative Addition Reactions," *J. Am. Chem. Soc.* **111**, 683 (1989); LBL-28051.
4. B.H. Weiller, E.P. Wasserman, R.G. Bergman, C.B. Moore, and G.C. Pimentel, "Time-Resolved IR Spectroscopy in Liquid Rare Gases: Direct Rate Measurement of an Intermolecular Alkane C-H Oxidative Addition Reaction," *J. Am. Chem. Soc.* **111**, 8188 (1989); LBL-28049.

LBL Reports

5. J.F. Hartwig, R.G. Bergman, and R.A. Andersen, "Mechanism of the C-C Cleavage of Acetone by the Ruthenium Benzyne Complex $(PMe_3)_4Ru(\eta^2-C_6H_4)$: Formation and Reactivity of an Oxametallacyclobutane Complex," submitted to *J. Am. Chem. Soc.*; LBL-28287.
6. E.P. Wasserman (Ph.D. Thesis), "Reactivity of Coordinatively Unsaturated Organometallic Species in the Gas Phase and in Solution," LBL-28052.

7. D.P. Klein (Ph.D. Thesis), "The Synthesis and Reactivity of Organoiridium Complexes Containing Metal-Heteroatom Bonds," LBL-28353.

Invited Talks

8. R.G. Bergman, "Activation of Alkanes Using Organotransition Metal Complexes," AAAS Meeting, San Francisco, CA, Jan. 16-17, 1989.
9. R.G. Bergman, "Activation of Carbon-Hydrogen Bonds in Alkanes Using Organometallic Complexes," Department of Chemistry, Occidental College, Los Angeles, CA, Jan. 27, 1989.
10. R.G. Bergman, "Using Kryptochemistry to Deal with Xenophobia: C-H Activation in Liquified Inert Gas Solvents," Department of Chemistry, Montana State University, Bozeman, Feb. 10, 1989; Department of Chemistry, University of Utah, Salt Lake City, Feb. 14, 1989; Department of Chemistry, University of Washington, Seattle, May 10, 1989.
11. R.G. Bergman, "Transformations of Organic Compounds Mediated by Organometallic Complexes," Symposium on Frontiers of Organic Chemistry, California Institute of Technology, Pasadena, Mar. 14-15, 1989.
12. R.G. Bergman, Series title: "The Use of Organotransition Metals in the Formation and Cleavage of Bonds Between Carbon and Hydrogen, Oxygen and Nitrogen"; "The Activation of Carbon-Hydrogen Bonds in Alkanes and Other Organic Molecules: Selectivity, Mechanism and Thermodynamics"; "Using Kryptochemistry to Deal with Xenophobia: C-H Activation in Liquified Inert Gas Solvents"; and "Models for Metal-Mediated Organic Oxidation Reactions: The Chemistry of Complexes with Metal-Oxygen and Metal-Nitrogen Bonds," Jonathan Mohrig Lectureship, Carleton College, Moorehead, MN, Apr. 17-21, 1989.
13. R.G. Bergman, "Oxidative Addition of C-H Bonds in Organic Molecules to Transition Metal Centers," Dalton Division Symposium, University of Hull, England, Apr. 4-7, 1989, LBL-27164.
14. R.G. Bergman, "Activation of Carbon-Hydrogen Bonds in Alkanes and Other Organic Molecules Using Organotransition Metal Complexes," NSF 8th Workshop on Reactive Intermediates, Rougemont, NC, May 13-15, 1989; 31st National Organic Symposium, Cornell University, Ithaca, NY, June 18-22, 1989.
15. R.G. Bergman, "Using Kryptochemistry to Deal with Xenophobia: C-H Activation in Liquified Noble Gas Solvents" and "Models for Metal-Mediated Organic Oxidation Reactions: The Chemistry of Complexes with Metal Oxygen and Metal-Nitrogen Bonds," 1989 Lind Lecturer, East Tennessee Section, ACS, Oct. 24-25, 1989.
16. R.G. Bergman, "Transformation of Organic Compounds using Organotransition Metal Complexes," Charles A. Stiefvater Memorial Lecture, University of Nebraska, Lincoln, Oct. 26, 1989.
17. "Models for Metal Mediated Oxidation Reactions: The Chemistry of Complexes with Metal-Heteroatom Bonds,"

Department of Chemistry, University of Washington, Seattle, Nov. 7-8, 1989.

18. R.G. Bergman, "Irreproducibility in the Scientific Literature: When do Scientists Tell the Whole Truth and Nothing but the Truth?" and "Models for Metal-Mediated Oxidation Reactions: The Chemistry of Complexes with Metal-Heteroatom Bonds," Department of Chemistry and Biochemistry, California State University, Los Angeles, Nov. 14, 1989.
19. R.G. Bergman, "Models for Metal-Mediated Organic Oxidation Reactions: The Chemistry of Complexes with Metal-Oxygen and Metal-Nitrogen Bonds," Department of Chemistry, University of California, San Diego, Dec. 4, 1989.
20. R.G. Bergman, "Exploratory and Mechanistic Investigations of Metal-Mediated Transformations of Organic Compounds" and "Transformation of Organic Compounds Induced by Heterodinuclear Complexes," PAC-Chem. Symposium, Honolulu, HI, Dec. 17-22, 1989.

HEAVY-ELEMENT CHEMISTRY

Actinide Chemistry*

Norman M. Edelstein, Richard A. Andersen, Kenneth N. Raymond, and Andrew Streitwieser, Jr., Investigators

INTRODUCTION

The purpose of this project is to study actinide materials in order to provide the basic knowledge necessary for their safe and economic utilization in present and future technology. The program includes the preparation of new gaseous, liquid, and solid phases and studies of their physical and chemical properties. Techniques for characterization include x-ray diffraction, optical and vibrational spectroscopy, magnetic resonance, and magnetic susceptibility. Equilibrium and kinetic data for complex formation are measured. From these complementary studies, new insights into the structural and chemical principles of actinide compounds are obtained with which to design new synthetic schemes to produce new materials.

A major aspect of the program is the design and synthesis of sequestering agents for actinide ions. These compounds are intended for use in the treatment of actinide poisoning and for possible application in the treatment of spent reactor fuels. Preparative, structural, and physical studies of new types of organoactinide, related organolanthanide, and new actinide inorganic complexes are continuing. Studies on optical spectra of actinide ions in crystals and in molecules are being pursued in order to understand their electronic structure.

SPECIFIC SEQUESTERING AGENTS FOR THE ACTINIDES

The coordination chemistry of the actinides, and related lanthanides, is being studied to provide the basis for new technological applications of these elements and to deal with the environmental problems posed by their past and present use.

*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

1. Removal of $^{238}\text{Pu(IV)}$ *in vivo* by Octadentate Ligands (Publication 3)

P.W. Durbin, D.L. White,[†] F.N. Jeung, F.L. Weill, L.C. Uhler, E. S. Jones, F.W. Bruenger,[‡] and K.N. Raymond

Previous work on *in vivo* chelation of 3,4,3-LICAMC has found that it removes approximately the same amount of ^{238}Pu from mice as $\text{CaNa}_3\text{-DTPA}$, but deposits some Pu in the kidneys and removes less Pu from the lungs. However, *in vitro* studies prove 3,4,3-LICAMC to be thermodynamically and kinetically superior to $\text{CaNa}_3\text{-DTPA}$. Information based on earlier work has been used to design the present experiments and to help account for this discrepancy. It has been determined that much of this past work *in vivo* has involved ligand contaminated by its methyl esters. *In vivo* testing of the pure ligand and its incompletely hydrolyzed esters found no significant difference in Pu removal.

Interpolation of literature values for protonation and formation constants of catechol monomers and their multidentate analogs with various metal ions, as well as the first pK's of the Pu-3,4,3-LICAMC complex, leads to the conclusion that *in vivo* none of the Pu-3,4,3-LICAMC complex exists as its most stable tetracatecholate complex. Temporary reduction of plasma and urine pH by injection of NH_4Cl significantly reduced Pu excretion, whereas pH elevation by injection of NaHCO_3 increased it. There was little influence on Pu deposition in the kidneys. Previous investigators showed deposition of Pu by 3,4,3-LICAMC complex in the more acidic environment of the kidneys. This parallels the failure to form a stable Pu-3,4,3-LICAMC complex in the aerated lungs, which are also acidic. Both observations are ascribed to the weak acidity of the LICAMC ligand.

The kinetics and thermodynamics involved in deprotonating the catechol hydroxyl, then, explain the differences in *in vivo* removal of Pu between 3,4,3-LICAMC and $\text{CaNa}_3\text{-DTPA}$.

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2. Removal of $^{238}\text{Pu}(\text{IV})$ from Mice by Polycatecholate, -Hydroxamate, or -Hydroxypyridinate Ligands (Publication 4)

P.W. Durbin, N. Jeung, S.J. Rodgers,[†] P.N. Turowski,[‡] F.L. Weill, D.L. White,^{||} and K.N. Raymond.

In vivo testing continues on octadentate ligands containing the 1-hydroxy-2-pyridone moiety. These data were compared to data previously published for 3,4,3-LICAMS, 3,4,3-LICAMC, and $\text{CaNa}_3\text{-DTPA}$.

All the present ligands have similarly shaped curves when plotted as Pu retention vs log ligand dosage. This similarity suggests that the ligands are removing Pu from the same pool, namely the circulating fluids. Injected 3,4,3-LIHOPO and 3,4,3-LICAMS removed the greatest amount of Pu; in addition, the amount removed was about the same for these ligands when administered orally, suggesting efficient and rapid absorption.

3,4,3-LIHOPO is also efficacious in removing deposited Pu from the liver and the skeleton.

DFOHOPO and $\text{Fe}(\text{III})$ -3,4,3-LIHOPO, unlike the desferri ligand, appear to have low toxicity. They have fast kinetics and should employ their full denticity at the full range of physiological pH values. They also are effective at low dosage, or when given 24 hr after Pu contamination. Both of these ligands merit further study.

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SYNTHETIC AND STRUCTURAL STUDIES OF ACTINIDES AND OTHER COMPOUNDS

3. Electron Transfer in Some Organouranium and Transuranium Systems (Publication 25)

D.C. Eisenberg, A. Streitwieser, and W.K. Kot

A reduced uranocene derivative, potassium bis([8]annulene)uranate(III), $\text{U}(\text{C}_8\text{H}_8)_2\text{K}$, and the 1,1'-dimethyl derivative are prepared by treatment of the corresponding uranocenes with potassium naphthalenide. Similarly, 1,1'-di-*t*-butylneptunocene(IV) and -plutonocene(IV) and the potassium salts of the corresponding reduced compounds have been prepared. The ^1H nuclear magnetic resonance (NMR) spectrum of the plutonocene shows temperature-independent paramagnetism (see Figure 3-1); the other compounds show normal temperature-

Figure 3-1. Proton NMR spectra of 1,1'-di-*t*-butylplutonocene. (XBL 883-1044)

dependent paramagnetism. Figure 3-2 shows the ^1H NMR spectrum of the lime-green reduction product, potassium bis(*t*-butyl[8]annulene)plutonate(III), in which the *t*-butyl peak shifts upfield as the temperature is lowered and the ring peaks shift downfield indicative of typical paramagnetic behavior. Mixtures of each of the bis[8]annuleneactinide(IV) compounds with the corresponding actinate(III) derivatives show rapid electron exchange on the NMR time scale.

4. Organolanthanide Catalysis of a Mukaiyama Addition Reaction (Publication 24)

L. Gong and A. Streitwieser

Bis[bis(1,3-trimethylsilyl)cyclopentadienyl] ytterbium(III) chloride, Cp^*YbCl , is an effective catalyst for the reaction of ketene silyl enolates, such as the trimethylsilyl enolate of methyl isobutyrate, with aldehydes, as shown in Figure 4-1. Reaction occurs in high yield at various temperatures. Facile reaction requires the presence of trimethylsilyl chloride and can be carried out with 0.01 moles of catalyst and at temperatures as low as -70°C . Aromatic aldehydes give yields typically over 80%, but

Figure 3-2. Proton NMR spectra of potassium bis(t-butyl[8]-annulene)plutonate(III). (XBL 883-1045)

aliphatic aldehydes give somewhat lower yields. The use of silyl enolates from propionic or phenylacetic esters gives high diastereoselectivity. An example for the phenylacetate reaction is shown in Figure 4-2.

The ytterbium catalyst is a dimer in inert solvents but forms a solvated monomer in donor solvents such as THF. Color changes and the infrared spectrum indicate that a complex with the aldehyde is formed, $\text{Cp}^*_2\text{YbClKOCHR}$, which undergoes rate-determining reaction with the silyl enolate to give a hypothesized internally coordinated Yb intermediate. The latter rapidly reacts with the TMSCl present to give the product, which is hydrolyzed on workup. This mechanism shown in Figure 4-3 is consistent with the kinetic observation that the rate is independent of the concentration of TMSCl so long as some is present.

The organolanthanide reagent thus shows promise as a useful addition to the growing armory of reagents for promoting stereo-controlled aldol-type addition reactions. With many possibilities for structural modification of the

Figure 4-1. A typical catalyzed Mukaiyama reaction. (XBL 903-931)

Figure 4-2. A stereochemical example. (XBL 903-932)

cyclopentadienyl ligands, the central lanthanide metal, and the leaving halide, much further refinement of the reagent is clearly possible.

5. Structural Studies on Cyclopentadienyl Compounds of Trivalent Cerium: Tetrameric $(\text{MeC}_5\text{H}_4)_3\text{Ce}$, Monomeric $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{Ce}$, and $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$, and their Coordination Chemistry (Publication 19)

S.D. Stults, R.A. Andersen, and A. Zalkin

The coordinated tetrahydrofuran in $(\text{MeC}_5\text{H}_4)_3\text{Ce}(\text{thf})$ can be removed by Me_3Al in a Lewis acid-base reaction or by the "toluene-reflux method" to give base-free $(\text{MeC}_5\text{H}_4)_3\text{Ce}$, which is a monomer in the gas phase though a tetramer in solid state; its crystal structure is monoclinic, $P2_1/a$, with $a = 12.497(5) \text{ \AA}$, $b = 26.002(8) \text{ \AA}$, $c = 9.664(3) \text{ \AA}$, $\beta = 97.33(3)^\circ$, $R = 0.041$ for 2117 data, and $F^2 > 2\sigma(F^2)$ (see Figure 5-1). The structure is made up of a cyclic tetramer in which two MeC_5H_4 rings are η^5 -bonded to each cerium atom and one MeC_5H_4 ring is bridging two cerium atoms such that the MeC_5H_4 ring is η^5 -bonded to one cerium and η^1 -bonded to the other. With larger cyclopentadienyl groups, the binary metallocenes ($\eta^5\text{-Me}_3\text{SiC}_5\text{H}_4$) $_3\text{Ce}$, ($\eta^5\text{-Me}_3\text{CC}_5\text{H}_4$) $_3\text{Ce}$, and [$\eta^5\text{-(Me}_3\text{Si)}_2\text{C}_5\text{H}_3$] $_3\text{Ce}$, are monomeric in gas phase and solid state. The structure of the latter is based upon a trigonal

Figure 4-3. Mechanism of the catalyzed Mukaiyama reaction. (XBL 903-933)

Figure 5-1 ORTEP diagram of $(\eta^5\text{-MeC}_5\text{H}_5)_2(\mu\text{-}\eta^5,\eta^5\text{-MeC}_5\text{H}_5)\text{Ce}_2$. 50% probability ellipsoids, Ce–C = 2.83(4) Å (avg.), Ce–ring centroid = 2.57 Å (avg.), and ring centroid–Ce–ring centroid = 129° (avg.). (XBL 8912 4438)

Figure 5-2 ORTEP drawing of $(\eta^5\text{-MeC}_5\text{H}_5)_3\text{Ce}$. 50% probability ellipsoids, Ce–C = 2.83(4) Å (avg.), Ce–ring centroid = 2.57 Å (avg.), and ring centroid–Ce–ring centroid = 129° (avg.). (XBL 8912 4438)

planar geometry; the crystals are monoclinic, $P2_1/c$, with $a = 22.752(5)$ Å, $b = 11.386(3)$ Å, $c = 17.431(4)$ Å, $\beta = 105.70(3)^\circ$, $R = 0.046$ for 2519 data, and $F^2 > 3\sigma(F^2)$ (see Figure 5-2). All of the binary metallocenes form 1:1 complexes with isocyanides and organocyanides, and the crystal structures of two of them have been done: $(\text{MeC}_5\text{H}_4)_3\text{Ce}(\text{CNCMe}_3)$ is monoclinic, $P2_1/c$, with $a = 14.259(3)$ Å, $b = 9.382(2)$ Å, $c = 17.652(3)$ Å, $\beta = 106.16(3)^\circ$, $R = 0.050$ for 1501 data, and $F^2 > 3\sigma(F^2)$; and $(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3)_3\text{Ce}(\text{CNCMe}_3)$ is also monoclinic, $P2_1/c$, with $a = 11.462(3)$ Å, $b = 17.146(4)$ Å, $c = 26.826(6)$ Å, $\beta = 112.93(3)^\circ$, $R = 0.047$ for 2457 data, and $F^2 > 3\sigma(F^2)$ (see Figures 5-3 and 5-4).

Figure 5-3 ORTEP drawing of $(\eta^5\text{-MeC}_5\text{H}_5)_3\text{Ce}(\text{CNCMe}_3)$. 50% probability ellipsoids, Ce–C(Cp) = 2.7(3) Å, Ce–ring centroid = 2.55 Å (avg.), ring centroid–Ce–ring centroid = 119° (avg.), Ce–C(19) = 2.71(2) Å, ring centroid–Ce–C(19) = 97° (avg.). (XBL 8912 4437)

Figure 5-4. ORTEP drawing of $[\eta^5-(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}(\text{CNCMe}_3)$; 50% probability ellipsoids; Ce-C(Cp) = 2.87(3) Å (avg.), Ce-ring centroid = 2.60 Å (avg.), ring centroid-Ce-ring centroid = 119.5° (avg.), Ce-C(34) = 2.70(1) Å, ring centroid-Ce-C(34) = 94° (avg.). (XBL 8912-4436)

6. Chemistry of Trivalent Cerium and Uranium Metallocenes: Reactions with Alcohols and Thiols (Publication 20)

S.D. Stults, R.A. Andersen, and A. Zalkin

The trivalent cerium metallocene, $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$, reacts with alcohols, HOR (R = CHMe₂ or Ph), or thiols, HSR (R = CHMe₂ or Ph), to give the dimers $(\text{Me}_3\text{CC}_5\text{H}_4)_4\text{Ce}_2(\mu\text{-ER})_2$, as shown by x-ray crystallography for the isopropoxide and isopropylthiolate derivatives. Crystals of $(\text{Me}_3\text{CC}_5\text{H}_4)_4\text{Ce}_2(\mu\text{-OCHMe}_2)_2$ are monoclinic, $P2_1/c$, with $a = 11.962(4)$ Å, $b = 14.489(5)$ Å, $c = 12.384(5)$ Å, $\beta = 103.31(3)^\circ$, and $V = 2089$ Å³; the structure was refined by full-matrix least squares to a conventional R-factor of 0.028, 2874 data, $F^2 > 2\sigma(F^2)$ (see Figure 6-1). The Ce₂O₂ unit is planar, the geometry about the cerium atom is pseudotetrahedral, and the geometry is planar about the oxygen atom. Crystals of $(\text{Me}_3\text{CC}_5\text{H}_4)_4\text{Ce}_2(\mu\text{-SCHMe}_2)_2$ are also monoclinic, $P2_1/m$, with $a = 14.255(9)$ Å, $b = 13.585(9)$ Å, $c = 11.265(7)$ Å, $\beta = 96.02(5)^\circ$, and $V = 2170$ Å³; the structure was refined by full-matrix least squares to a conventional R-factor of 0.028, 2899 data, $F^2 > 2\sigma(F^2)$ (see Figure 6-2). The Ce₂S₂ unit is planar and the geometry about cerium is pseudotetrahedral, though the geometry is pyramidal at sulfur so that the isopropyl groups are anti relative to the Ce₂S₂ ring. Methanol or water gives an insoluble solid, presumably Ce(OMe)₃ or Ce(OH)₃, whereas HECMe₃ (E = O or S) does not react with $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$, but the thiol

Figure 6-1. ORTEP diagram of $(\text{Me}_3\text{CC}_5\text{H}_4)_4\text{Ce}_2(\mu\text{-OCHMe}_2)_2$; 50% probability ellipsoids; C(19) is disordered and refined as two isotropic half-atoms, only one conformation of which is shown. Ce-C (avg.) = 2.83 ± 0.04 Å; Ce-Cp (cent.) = 2.58 Å; Ce-O = 2.373(3) Å, 2.369(3) Å; Ce...Ce = 3.844(2) Å; Ce-O-Ce = 108.3(1)°; O-Ce-O = 71.7(1)°; Ce-O-C(19) = 143.3(5)°, 108.2(5)°; Cp (cent.)-Ce-Cp (cent.) = 128.5°. (XBL 8912-4435)

does react with the sterically less bulky metallocene $(\text{MeC}_5\text{H}_4)_3\text{Ce}(\text{thf})$ to give $(\text{MeC}_5\text{H}_4)_4\text{Ce}_2(\mu\text{-SCMe}_3)_2$. The pK_a's (H₂O) of the organic acids generally predict the thermodynamic outcome of the proton exchange reactions, though the latter set of experiments shows that kinetic (i.e., steric) factors play a role. The uranium metallocene, $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{U}$, reacts with HSPh at low temperature to give isolable $(\text{Me}_3\text{CC}_5\text{H}_4)_4\text{U}_2(\mu\text{-SPh})_2$, which rearranges in solution to the monomeric, tetravalent species $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{USPh}$ and unidentified material. The dimeric intermediate cannot be detected with the sterically smaller metallocene $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$, as only $(\text{MeC}_5\text{H}_4)_3\text{UER}$ (ER = OMe, OCHMe₂, OPh, and SCHMe₂) is isolated.

Figure 6-2. ORTEP diagram of $(\text{Me}_3\text{CC}_5\text{H}_4)_4\text{Ce}_2(\mu\text{-SCHMe}_2)_2$; 50% probability ellipsoids. Ce-C (avg.) = 2.78 ± 0.02 Å; Ce-Cp (cent.) = 2.52 Å; Ce-S = 2.870(2), 2.894(2) Å; Ce...Ce = 4.449(2) Å; Ce-S-Ce = 101.06(6)°; S-Ce-S = 78.94(6)°; Ce-S-C(19) = 128.5(3)°, 118.2(4)°; Cp (cent.)-Ce-Cp (cent.) = 131°. (XBL 8912-4434)

7. $(\text{Me}_5\text{C}_5)_2\text{Yb}_2(\mu\text{-PPh})_2(\text{thf})_4$, a Compound with a Bridging Phosphide Ligand and an Agostic $\text{Yb}\cdots\text{H-P}$ Interaction (Publication 21)

D.J. Berg, R.A. Andersen, and A. Zalkin

Phenylphosphine reacts with $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$ to give $\text{Me}_5\text{C}_5\text{H}$ and $(\text{Me}_5\text{C}_5)_2\text{Yb}_2(\mu\text{-PPh})_2(\text{thf})_4$. Crystals of the ytterbium compound are monoclinic, $P2_1/c$, with $a = 8.981(2)$ Å, $b = 14.630(2)$ Å, $c = 19.081(3)$ Å, and $\beta = 98.53(2)^\circ$. The structure was refined by full-matrix least squares to a conventional R-factor of 0.048, 3124 data, $F^2 > 2\sigma(F)^2$ (see Figure 7-1). The crystal structure shows that the two $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{thf})_2$ centers are asymmetrically bridged by phenylphosphide groups with Yb-P distances of 2.959(2) Å and 3.068(2) Å. The asymmetry in the bridge is the result of a short, 1.86(6) Å, $\text{Yb}\cdots\text{H}$ interaction (the hydrogen atom was located in the x-ray study and refined isotropically), which is correlated with the longer Yb-P distance. This type of $\text{Yb}\cdots\text{H-P}$ interaction has not been observed previously in bridging phosphide compounds. Though PhPH_2 reacts with $(\text{Me}_5\text{C}_5)_2\text{Yb}$ by way of a proton-transfer reaction, cyclohexylphosphine, p-toluidine, or ammonia give 1:1 coordination compounds. These results are explained by the pK_a 's of the protic acids relative to the pK_a of $\text{Me}_5\text{C}_5\text{H}$.

Figure 7-1. ORTEP drawing of $(\text{Me}_5\text{C}_5)_2\text{Yb}_2(\mu\text{-PPh})_2(\text{thf})_4$; 50% probability ellipsoids. The hydrogen atom on phosphorus is refined isotropically, and all other non-hydrogen atoms were refined anisotropically. The molecule contains a crystallographic center of inversion located in the center of the Yb_2P_2 rhombus so that the labelled atoms are related to the unlabeled or primed atoms by the center of inversion. (XBL 8912-4433)

8. Trivalent Uranium Chemistry: Molecular Structure of $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{U}$ (Publication 22)

J.L. Stewart and A. Andersen

The crystal structure of $[\text{U}(\text{N}(\text{SiMe}_3)_2)_3] \cdot 1/3(\text{C}_6\text{H}_{12})$ at -110°C (space group $P\bar{3}1c$, $a = b = 16.370(2)$ Å, $c = 8.302(1)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, $V = 1926.7(1)$ Å³, $Z = 2$) shows that the monomeric complex is pyramidal at uranium with $\text{U-N} = 2.320(4)$ Å and $\text{N-U-N} = 116.24(7)^\circ$ (see Figure 8-1). The pyramidal geometry is rationalized by the purely ionic model, the polarized-ion model. The magnetic susceptibility from 35 to 280 K gives $\mu(\text{eff}) = 3.35$ B.M. ($\theta = -13$ K).

Figure 8-1. ORTEP diagram down the $\bar{3}$ -axis of $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{U} \cdot 1/3(\text{C}_6\text{H}_{12})$ at -110°C ; 50% thermal ellipsoids, showing one of the two disordered uranium sites. $\text{U-N} = 2.320(4)$ Å, $\text{N-Si} = 1.713(1)$ Å, $\text{N-U-N} = 116.24(7)^\circ$, $\text{Si-N-Si} = 125.8(2)^\circ$. (XBL 8912-4432)

PHYSICAL AND SPECTROSCOPIC PROPERTIES

9. $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2[\mu\text{-}1,4\text{-N}_2\text{C}_6\text{H}_4]$: a Bimetallic Molecule with Antiferromagnetic Coupling Between the Uranium Centers (Publication 28)

R.K. Rosen,[†] R.A. Andersen, and N.M. Edelstein

The two bimetallic, pentavalent uranium metallocene compounds $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2(\mu\text{-}1,4\text{-N}_2\text{C}_6\text{H}_4)$, **1**, and $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2(\mu\text{-}1,3\text{-N}_2\text{C}_6\text{H}_4)$, **2**, have been prepared from $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ and 1,4-diazo- and 1,3-diazo-benzene, respectively, at room temperature. Magnetic susceptibility studies on these solids from 5 to 280 K show that the spins on **1** antiferromagnetically couple at ~ 20 K, while those on **2** do not couple to 5 K (see Figure 9-1). The susceptibility curve for **1** can be fit to a one-dimensional Ising model with a calculated J of $\sim 19 \text{ cm}^{-1}$, as shown in Figure 9-2. A super-exchange model is postulated to account for these results, since the imido-nitrogens of the bridging ligand in **1** are in the 1,4-positions of the benzene ring and they can conjugate, while the bridging ligand in **2** has the imido-nitrogen on the 1,3-positions of the benzene ring and they cannot conjugate. This work is the first example of antiferromagnetic coupling between two metal ions in an actinide bimetallic molecular system.

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Figure 9-1. Experimental magnetic susceptibility data of **1** and **2** as a function of temperature. (XBL 901-210)

Figure 9-2. Comparison of experimental magnetic susceptibility data with calculated values for **1**. The calculations are with $g_{\parallel} = 2.6$. The impurity is assumed to be $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$, and three calculated curves are shown for $J = -18 \text{ cm}^{-1}$ (no impurity), $J = -19 \text{ cm}^{-1}$ (1 mole% impurity), and $J = -20 \text{ cm}^{-1}$ (2 mole% impurity). (XBL 901-211)

10. Powder Neutron Diffraction and Magnetic Susceptibility of $^{248}\text{CmO}_2$ (Publication 18)

L.R. Morss,[†] J.W. Richardson, Jr.,[†] C.W. Williams,[†] G.H. Lander,[‡] A.C. Lawson,^{||} N.M. Edelstein, and G.V. Shalimoff

The first neutron-diffraction experiments on a sample of ~ 55 mg of CmO_2 using the rare isotope ^{248}Cm are reported. Preparative techniques have assured that the sample is close to stoichiometry, and x-ray patterns show only the expected fcc lines. The neutron-diffraction experiments confirm that the sample is nearly stoichiometric and rule out the possibility that the oxygen atoms form a superlattice to accommodate a mixture of Cm^{3+} and Cm^{4+} ions. Cm^{3+} ions should have a temperature-dependent paramagnetic susceptibility of $\sim 8.0 \text{ BM}$, while Cm^{4+} ions are expected to have a temperature-independent susceptibility whose value is less than $650 \times 10^{-6} \text{ emu/mol}$. Magnetic susceptibility measurements as a function of temperature give a value of $\sim 3.4 \mu_B$ for the effective paramagnetic moment, consistent with many other determinations of this property in CmO_2 , which have been interpreted in the past as indicating $\sim 18\%$ Cm^{3+} impurity. In view of the contradiction between bulk susceptibility on the one hand, and thermogravimetric and diffraction results on the other, a re-evaluation of the electronic ground states in the actinide dioxides may be needed. Some other contradictory experimental results are given.

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11. Doubly Resonant Coherent Anti-Stokes Raman Spectroscopy of Ce^{3+} in LuPO_4 (Publication 29)

D. Piehler and N. Edelstein

We have measured coherent anti-Stokes Raman spectra between crystal-field levels of the $^2F_{5/2}$ and $^2F_{7/2}$ manifolds of the Ce^{3+} ion diluted in LuPO_4 at ~ 10 K. By using a frequency-tripled $\text{Nd}^{3+}:\text{YAG}$ laser ($28,192\text{ cm}^{-1}$) and a tunable dye laser operating in the $26,000\text{ cm}^{-1}$ range, we have satisfied two resonance conditions. When the difference in energy between the two lasers is equal to the energy of the lower crystal-field levels of the $^2F_{7/2}$ manifold, the coherent anti-Stokes Raman spectroscopy (CARS) signal will be in the $30,400\text{ cm}^{-1}$ range, less than 100 cm^{-1} below the lowest $5d^1$ band (see Figure 11-1). Thus, the anti-Stokes signal is nearly resonant with the lowest crystal-field level of the $5d^1$ configuration of Ce^{3+} at $30,460\text{ cm}^{-1}$. For a LuPO_4 crystal doped with 0.06 mol% Ce^{3+} , we found enhancements of the third-order susceptibility, $|\chi^{(3)\text{R}}/\chi^{(3)\text{NR}}|$, as high as 11.6 (see Figure 11-2). This enhancement is over 20 times larger than that seen previously in singly resonant CARS experiments with pure rare-earth crystals.

Figure 11-1. Schematic diagram of doubly resonant CARS in $\text{Ce}^{3+}:\text{LuPO}_4$. $\omega_1/2\pi = 28,192\text{ cm}^{-1}$, $\omega_2/2\pi = 26,013\text{ cm}^{-1}$, $(2\omega_1 - \omega_2)/2\pi = 30,371\text{ cm}^{-1}$, $\Delta = 89\text{ cm}^{-1}$, and $D = 2268\text{ cm}^{-1}$. (XBL 901-208)

Figure 11-2. Intensity of CARS signal at $|\chi^{(3)\text{R}}/\chi^{(3)\text{NR}}|^2$ at frequency ω_3 as a function of $\omega_1 - \omega_2$ normalized to the off resonance intensity. The solid line is a fitted curve. (XBL 901-209)

12. Contributions from the Energy-Level Structure of the $4f^{11}5d^1$ Intermediate Configuration to the Electronic Raman Scattering Intensities of TmPO_4 (Publication 17)

S. Xia,[†] G.M. Williams,[‡] and N.M. Edelstein

A direct calculation of the electronic Raman scattering intensities of TmPO_4 , which includes the detailed energy-level structure of the intermediate excited configuration $4f^{11}5d^1$, is given. The contributions to the scattering intensities from various perturbations within the $4f^{11}5d^1$ configuration are enumerated. Most of the calculated relative scattering intensities are improved when compared to the results of the conventional Judd-Ofelt-Axe calculations. However, there are significant differences remaining between the experimental and calculated intensities.

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13. Excitation Profiles of Resonance Electronic Raman Scattering in ErPO_4 Crystals (Publication 13)

G.M. Williams,[†] P.C. Becker,[‡] N. Edelstein, L.A. Boatner,^{||} and M.M. Abraham^{||}

The intensities of electronic Raman scattering transitions between the ground and excited crystal-field states of the ground $^4I_{15/2}$ multiplet of Er^{3+} in crystals of ErPO_4 were measured as a function of excitation frequency in the region of an intermediate-state resonance between the $^4I_{15/2}$ ground state and a crystal-field state of the $^4F_{7/2}$ multiplet. For excitation frequencies near the intermediate-state resonance, the observed spectra are the result of electronic Raman scattering and are not due to absorption followed by fluorescence (see Figure 13-1). No such determination could be made for direct resonance excitation. Enhancements of the intensities of the electronic Raman scattering by a factor on the order of 100 are reported (see Figure 13-2). The electronic Raman scattering excitation profiles (excitation frequency versus enhancement) are found to be asymmetric in excitation frequency about the resonance. These profiles can be accurately modeled using standard electronic Raman intensity theory and the measured oscillator strengths and linewidths of the $^4I_{15/2} \rightarrow ^4F_{7/2}$ one-photon transitions.

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Figure 13-1. Frequency shifts of the peaks in the YXZ_2X spectra of ErPO_4 as a function of excitation frequency. The horizontal lines are expected locations of Raman peaks. The skewed lines are expected locations of fluorescence peaks. (XBL 901-219)

Figure 13-2. Measured excitation profiles. The large decrease in the center of the figure is due to the absorption of the incident laser light by the resonant transition $0 \text{ cm}^{-1} \rightarrow 20,492.9 \text{ cm}^{-1}$. Top: excitation profile for the $\Delta = 303 \text{ cm}^{-1}$ vibrational Raman scattering. Middle: excitation profile for the $\Delta = 33 \text{ cm}^{-1}$ electronic Raman scattering. Bottom: excitation profile for the $\Delta = 53 \text{ cm}^{-1}$ electronic Raman scattering. For all the cases, the scattering geometry was YXZ_2X . (XBL 901-218)

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. K.N. Raymond and T.M. Garrett, "Sequestering Agents Specific for High Oxidation State Cations," *Pure Appl. Chem.* **60**, 1807 (1988); LBL-28309.

2. K.N. Raymond, "Template Synthesis of Ligands for Highly Charged Metal Cations," *J. Incl. Phenom.* **7**, 169, (1989); LBL-28310.
3. P.W. Durbin, D.L. White, N. Jeung, F.L. Weigl, L.C. Uhler, E.S. Jones, F.W. Bruenger, and K.N. Raymond, "Chelation of $^{238}\text{Pu}(\text{IV})$ *in vivo* by 3,4,3-LICAM(C): Effects of Ligand Methylation and pH," *Health Phys.* **56**, 839 (1989); LBL-23564(1/2).
4. P.W. Durbin, N. Jeung, S.P. Rodgers, P.N. Turowski, F.L. Weigl, D.L. White, and K.N. Raymond, "Removal of $^{238}\text{Pu}(\text{IV})$ from Mice by Polycatechoylate, -Hydroxamate or -Hydroxypyridinate Ligands," *Rad. Prot. Dos.* **26**, 351 (1989); LBL-28311.
5. C.J. Burns and R.A. Andersen, "Reaction of $(\text{Me}_5\text{C}_5)_2\text{Yb}$ with Fluorocarbons: Formation of $(\text{Me}_5\text{C}_5)_4\text{Yb}_2(\mu\text{-F})$ by Intramolecular C-F Activation," *J. Chem. Soc. Chem. Comm.*, 136 (1989); LBL-26006.
6. S.D. Stults, R.A. Andersen, and A. Zalkin, " $[\text{Li}(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2)_2][\text{Li}_2(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2)_2(\mu\text{-}\eta^5, \eta^5\text{-MeC}_5\text{H}_4)] [(\eta^5\text{-MeC}_5\text{H}_4)_6\text{U}_2(\mu\text{-Me})_2]$: A Compound with Symmetrically Bridging MeC_5H_4 and Me Groups," *J. Am. Chem. Soc.* **111**, 4507 (1989); LBL-26155.
7. D.J. Berg, C.J. Burns, R.A. Andersen, and A. Zalkin, "Electron-Transfer Reactions of Divalent Ytterbium Metallocenes. Synthesis of the Series $[(\text{Me}_5\text{C}_5)_2\text{Yb}]_2[\mu\text{-E}]$ (E = O, S, Se, or Te) and Crystal Structure of $[(\text{Me}_5\text{C}_5)_2\text{Yb}]_2[\mu\text{-Se}]$," *Organometallics* **8**, 1865 (1989); LBL-22934.
8. M.H. Lyth, A. Streitwieser, and M.J. Miller, "1,5-Disubstituted Cyclooctatetraenes," *J. Org. Chem.* **54**, 2331 (1989); LBL-26326.
9. D.C. Eisenberg, S.A. Kinsley, and A. Streitwieser, "Electron Exchange Between Dipotassium Bis([8]annulene)ytterbate(II) and Potassium Bis([8]annulene)ytterbate(III)," *J. Am. Chem. Soc.* **111**, 5769 (1989); LBL-25585.
10. I.S. Poirot, W.K. Kot, N.M. Edelstein, M.M. Abraham, C.B. Finch, and L.A. Boatner, "Optical Study and Analysis of Pu^{4+} in Single Crystals of ZrSiO_4 ," *Phys. Rev. B* **39**, 6388 (1989); LBL-25729.
11. D.M. Anderson, F.G.N. Cloke, P.A. Cox, N. Edelstein, J.C. Green, T. Pang, A.A. Sameh, and G. Shalimoff, "On the Stability and Bonding in Bis(η -arene)lanthanide Complexes," *J. Chem. Soc., Chem. Commun.* **1**, 53 (1989); LBL-26402.
12. H.-D. Amberger, H. Schultze, H. Reddmann, G.V. Shalimoff, and N.M. Edelstein, "The Electronic Structure of Organometallic Complexes of the f Elements XXIII. Interpretation of the Magnetochemical and Optical Data of a Tetrahydrofuran Adduct Derived From $\text{Tris}(\eta^5\text{-cyclopentadienyl})\text{-ytterbium}(\text{II})$," *J. Less Common Metals* **149**, 249 (1989); LBL-25354.
13. G.M. Williams, P.C. Becker, N. Edelstein, L.A. Boatner, and M.M. Abraham, "Excitation Profiles of Resonance Electronic Raman Scattering in ErPO_4 Crystals," *Phys. Rev. B* **40**, 1288 (1989); LBL-26351.
14. G.M. Williams, P.C. Becker, J.C. Conway, N. Edelstein, L.A. Boatner, and M.M. Abraham, "Intensities of Electronic Raman Scattering between Crystal-Field Levels of Ce^{3+} in LuPO_4 : Nonresonant and Near-resonant Excitation," *Phys. Rev. B* **40**, 4132 (1989); LBL-26350.
15. G.M. Williams, N. Edelstein, L.A. Boatner, and M.M. Abraham, "Anomalous Small 4f-5d Oscillator Strengths and 4f-4f Electronic Raman Scattering Cross Sections for Ce^{3+} in Crystals of LuPO_4 ," *Phys. Rev. B* **40**, 4143 (1989); LBL-26348.
16. W.K. Kot, G.V. Shalimoff, N.M. Edelstein, M.A. Edelman, and M.F. Lappert, " $[\text{ThIII}(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)_3]$, An Actinide Compound with a $6d^1$ Ground State," *J. Am. Chem. Soc.* **110**, 986 (1988); LBL-24136.
17. S. Xia, G.M. Williams, and N.M. Edelstein, "Contributions From the Energy Level Structure of the $4f^{11}5d^1$ Intermediate Configuration to the Electronic Raman Scattering Intensities of TmPO_4 ," *Chem. Phys.* **138**, 255 (1989); LBL-26122.
18. L.R. Morss, J.W. Richardson, Jr., C.W. Williams, G.H. Lander, A.C. Lawson, N.M. Edelstein, and G.V. Shalimoff, "Powder Neutron Diffraction and Magnetic Susceptibility of $^{248}\text{CmO}_2$," *J. Less Common Metals* **156**, 273 (1989); LBL-28438.

LBL Reports

19. S.D. Stults, R.A. Andersen, and A. Zalkin, "Structural Studies on Cyclopentadienyl Compounds of Trivalent Cerium: Tetrameric $(\text{MeC}_5\text{H}_4)_3\text{Ce}$, Monomeric $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{Ce}$ and $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$ and Their Coordination Chemistry," LBL-26279.
20. S.D. Stults, R.A. Andersen, and A. Zalkin, "Chemistry of Trivalent Cerium and Uranium Metallocenes: Reactions with Alcohols and Thiols," submitted to *Organometallics*; LBL-27041.
21. D.J. Berg, R.A. Andersen, and A. Zalkin, " $(\text{Me}_5\text{C}_5)_2\text{Yb}_2(\mu\text{-PPh})_2(\text{thf})_4$, a Compound with a Bridging Phosphide Ligand and an Agostic Yb-H-P Interaction," submitted to *J. Am. Chem. Soc.*; LBL-27107.
22. J.L. Stewart and R.A. Andersen, "Trivalent Uranium Chemistry: Molecular Structure of $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{U}$," submitted to *Inorg. Chem.*; LBL-27499.
23. R.K. Rosen (Ph.D. Thesis), "Reaction of $\text{Tris}(\text{cyclopentadienyl})\text{uranium}$ Compounds with Amines, Azides, and Related Ligands," LBL-28271.
24. L. Gong and A. Streitwieser, "Organolanthanide Catalysis of a Mukaiyama Addition Reaction," submitted to *J. Am. Chem. Soc.*; LBL-27759.
25. D.C. Eisenberg, A. Streitwieser, and W.K. Kot, "Electron Transfer in Some Organouranium and Transuranium Systems," *Inorg. Chem.* (in press); LBL-26933.
26. L. Gong (Ph.D. Thesis), "Organolanthanide Reagents and the Mukaiyama Reaction," LBL-26680.
27. J.T. Rigsbee, Jr. (Ph.D. Thesis), "[8]Annulene Derivatives of Cerium," LBL-28289.
28. R.K. Rosen, R.A. Andersen, and N.M. Edelstein, " $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2[\mu\text{-1,4-N}_2\text{C}_6\text{H}_4]$: A Bimetallic Molecule with Antiferromagnetic Coupling Between the Uranium Centers," submitted to *J. Am. Chem. Soc.*; LBL-28093.

29. D. Piehler and N. Edelstein, "Doubly Resonant Coherent Anti-Stokes Raman Spectroscopy of Ce^{3+} in LuPO_4 ," *Phys. Rev. A* (in press); LBL-28203.
30. R.K. Rosen, D.J. Berg, J.M. Boncella, R.A. Andersen, and N.M. Edelstein, "Electron Exchange Across Bridging Ligands in Binuclear Complexes of the f-Block Metals," LBL-28234abs.
31. N. Edelstein, "Optical and Magnetic Properties of the Transuranium Elements," LBL-28235abs.
32. N. Edelstein, W. Kot, D. Piehler, G. Shalimoff, D. Ball, M.M. Abraham, C.B. Finch, and L.A. Boatner, "Optical and EPR Spectra of Trivalent Actinides Diluted in LuPO_4 ," LBL-28236abs.

Invited Talks

33. K.N. Raymond, "Spectroscopy and Structure of Iron Siderophores," Pacific Conference on Chemistry and Spectroscopy, San Francisco, CA, Oct. 27, 1988.
34. K.N. Raymond, "Metal Ions in Bondage — From Nature to the Unnatural," DuPont Distinguished Lecturer, Indiana University, Bloomington, Nov. 2, 1988.
35. K.N. Raymond, "Sequestration of the Lanthanide and Actinide Elements," Fishel Lecturer, Vanderbilt University, Nashville, TN, Nov. 3, 1988.
36. K.N. Raymond, "Specific Sequestering Agents for Higher Oxidation State Metal Cations—Molecular Bondage," University of California, Los Angeles, Dec. 1, 1988.
37. K.N. Raymond, "Sequestering Agents for the Lanthanides and Actinides—f Elements in Bondage," Florida State University, Tallahassee, Dec. 9, 1988.
38. K.N. Raymond, "Redox Properties and Release Kinetics of Fe(III) in Transferrin," Gordon Conference, Ventura, CA, Jan. 23–27, 1989.
39. K.N. Raymond, "Metal-Ion Sequestering Agents: Ions in Bondage," University of California, Santa Cruz, Apr. 10, 1989.
40. K.N. Raymond, "Coordination Chemistry: From Biology to Metal Ion Bondage" and "Microbial Geritol: Siderophore Mediated Iron Transport," Degussa Distinguished Research Chemist Series Speaker, University of South Alabama, Mobile, Apr. 13–14, 1989.
41. K.N. Raymond, "Metal Ions in Bondage," University of Chicago, Chicago, IL, May 15, 1989.
42. K.N. Raymond, "Coordination Chemistry Adventures of Glyphosate" and "Specific Sequestering Agents for High Oxidation Metal Ions," Monsanto Co., St. Louis, MO, May 22, 1989.
43. K.N. Raymond, "Siderophore Mediated Iron Transport: Microbes as Coordination Chemists," University of Queensland, Brisbane, Australia, July 17, 1989.
44. K.N. Raymond, "Specific Sequestering Agents: Metal Ions in Bondage," University of Queensland, Brisbane, Australia, July 18, 1989.
45. K.N. Raymond, "The Glyphosate Wars," University of Queensland, Brisbane, Australia, July 19, 1989.
46. K.N. Raymond, "Biological Iron Storage and Transport: Transferrin Chemistry," University of Queensland, Brisbane, Australia, July 20, 1989.
47. R.A. Andersen, "Studies in f-Element Chemistry," Organometallic Workshop, University of California, San Diego, May 23, 1989; Technical University of Berlin, Federal Republic of Germany, May 5–6, 1989; University of Cardiff, Wales, United Kingdom, Sept. 20, 1989.
48. A. Streitwieser, "f-Element Organometallic Chemistry," Department of Chemistry, Cornell University, Ithaca, NY, Oct. 9, 1989; Department of Chemistry, Northern Illinois University, DeKalb, Oct. 16, 1989; Department of Chemistry, University of Illinois, Urbana, Oct. 17, 1989.
49. A. Streitwieser, "Discovery of Uranocene—Sandwiches, Half-sandwiches, and f Element Organometallic Chemistry," Department of Chemistry, California Polytechnic University at Pomona, Nov. 15, 1989.
50. N.M. Edelstein, "Recent Results in Thorium, Protactinium, and Uranium Chemistry," Laboratoire de Reactivite et Mecanismes en Chimie Inorganique, CEA, Saclay, France, Sept. 22, 1989; University of Sussex, England, Oct. 18, 1989.
51. N.M. Edelstein, "Optical and Magnetic Properties of the Transuranium Elements," 1989 International Chemical Congress of Pacific Basin Societies, Honolulu, HI, Dec. 18, 1989.

CHEMICAL ENGINEERING SCIENCES

Molecular Thermodynamics for Phase Equilibria in Mixtures*

John M. Prausnitz, Investigator

INTRODUCTION

Phase equilibria are required for design of efficient, large-scale separation processes (e.g., distillation and extraction) in the chemical and related industries. In this context, "efficient" refers to optimum use of raw materials and to conservation of energy.

Since the variety of technologically important fluid mixtures is extremely large, it is not possible to obtain all desired equilibria from experiment. Therefore, the objective of this research is the development of molecular thermodynamics for interpretation and correlation of selected representative phase-equilibrium data toward reliable prediction of phase equilibria for computer-aided engineering design. The correlations are expressed through semitheoretical physicochemical models. In this research, particular attention is given to those systems that are of interest in energy-related industries, especially those concerned with fossil fuels, aqueous mixtures containing electrolytes, fossil-fuel/water mixtures, and mixtures encountered in the production of chemicals, especially polymers.

Development of molecular thermodynamics calls for a combination of theoretical computations and experimental work. Further, it demands simultaneous awareness, first, of progress in molecular science, and second, of realistic requirements for engineering design.

1. Solubilities of n-Octadecane, Phenanthrene, and n-Octadecane/Phenanthrene Mixtures in Supercritical Propane at 390 and 420 K and Pressures to 60 bar (Publication 1)

D. Dimitrelis and J.M. Prausnitz

Solubility data were obtained for n-octadecane, phenanthrene, and a nearly equimolar n-octadecane-phenanthrene mixture in supercritical propane. Solubilities were measured in a flow apparatus at 390 and 420 K over the pressure range 35–60 bar. The experimental data have been correlated using the perturbed-hard-chain equation of state. Agreement between experiment and correlation is good.

2. Liquid-Liquid Equilibria for Binary and Ternary Systems Including the Critical Region. Transformation to Nonclassical Coordinates (Publication 2)

J.J. de Pablo and J.M. Prausnitz

Classical constitutive equations for equilibrium processes are inaccurate near the critical point. To improve the performance of classical models near the critical point of a pure fluid, Fox, in 1983, proposed a method for transforming the coordinates of a classical equation of state to nonclassical coordinates.¹ In this work, the method of Fox is extended and applied to binary liquid mixtures at constant pressure and to ternary liquid mixtures at constant temperature and pressure. A conventional activity-coefficient model is used to represent mixture properties; mixture parameters are determined primarily from the experimental (or estimated) critical point and stability conditions. Results are shown for binary and ternary liquid mixtures. The method proposed here gives good representation of liquid-liquid equilibria, including the critical region. However, the required calculations are complex, and therefore, a phenomenological method presented earlier may be preferred for engineering calculations.

*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

1. J. Fox, *Fluid Phase Equilib.* **14**, 45 (1983).

3. Thermodynamics of High-Pressure Aqueous Systems Containing Gases and Salts (Publication 3)

A.H. Harvey and J.M. Prausnitz

This work provides a new method for calculating phase equilibria for systems where conventional activity-coefficient models are not suitable. A procedure is presented for superimposing ionic effects on a conventional equation of state for nonelectrolytes. A modification of Born's equation is used to describe charging the ions; ion-ion interactions are described with the mean spherical approximation, coupled with an adjustable salt/solvent parameter that is obtained from osmotic-coefficient data at room temperature. The equation of state is used to predict gas solubilities in aqueous salt solutions at high pressures. While this method produces qualitative agreement with the experimental solubility data, quantitative agreement requires a salt/gas parameter obtained from Setschenow-constant data. When Setschenow constants are used, agreement with experiment is good except at high salt concentrations, where salting-out is usually underpredicted. Good results are obtained for phase equilibria in a natural-gas/brine system at high pressures.

4. Thermodynamics of Concentrated Electrolyte Solutions (Publication 4)

Y. Liu, A.H. Harvey, and J.M. Prausnitz

A new equation is derived for the activity coefficient of an electrolyte in a liquid solvent (such as water) as a function of electrolyte concentration. This equation contains contributions from long-range electrostatic forces and from short-range attractive forces; it holds from high dilution to the saturation limit. The new equation is based on extended Debye-Hückel theory for long-range effects and the local-composition concept for short-range effects. For a single-electrolyte solution, the new equation contains only one adjustable energy parameter and three other parameters that are ion-specific, not electrolyte-specific. Therefore, extension to multicomponent electrolyte solutions follows without additional assumptions. Ion-specific parameters are reported for H^+ , K^+ , Li^+ , Br^- , and

Cl^- ions. Calculated and experimental activity coefficients are in excellent agreement for aqueous solutions of HBr , HCl , KCl , $LiBr$, and $LiCl$.

5. A Phenomenological Correction to an Equation of State for the Critical Region (Publication 5)

G.F. Chou and J.M. Prausnitz

This work represents a phenomenological correction to improve a classical equation of state for representing phase equilibria and densities in the vapor-liquid critical region. This correction consists of two steps. The first step is a volume translation that locates the correct critical point; this volume translation also improves density predictions for pure fluids and mixtures. The second step provides a near-critical contribution to the residual Helmholtz energy, which accounts for anomalous behavior near the critical point. For pure fluids, the near-critical contribution flattens the coexistence curve and pressure-density isotherms near the critical point. For mixtures, the near-critical contribution has only a small effect on the calculated coexistence curve; this effect is often masked by the choice of binary interaction parameters in the classical equation that have a more profound effect on the results.

6. Mutual Solubilities of Water and Hydrocarbons from an Equation of State. Need for an Unconventional Mixing Rule (Publication 6)

S. Michel, H.H. Hooper, and J.M. Prausnitz

For calculating mutual solubilities of water and hydrocarbons with an equation of state, none of the conventional mixing rules are satisfactory for engineering calculations. Based on recent experimental data, an unconventional modification is introduced into the usual quadratic mixing rule for attractive-energy parameter a ; this modification represents the well-studied hydrophobic effect. For the temperature range 20–200°C, quantitative description of mutual solubilities in binary systems is obtained with three binary parameters. Attempts to correlate these parameters with molecular properties were only partly successful.

7. The Nonadditive Hard-Sphere Mixture as a Reference System in Equation-of-State Calculations (Publication 7)

A.H. Harvey and J.M. Prausnitz

A new reference system is presented for equation-of-state (EOS) calculations for highly asymmetric mixtures. This system allows the introduction of an adjustable binary parameter in the reference term of the EOS while preserving the Boublik-Mansoori mixed-hard-sphere form, which is advantageous for mixtures whose components differ greatly in size. The new reference term is tested against a one-fluid reference term of the Carnahan-Starling form; in each case the EOS used one adjustable parameter in the reference term and one in the perturbation term. For binary systems, the new method offers little improvement over the one-fluid theory. However, when binary parameters are used to predict multicomponent vapor-liquid equilibria, the new method may have some advantages.

8. A Cubic Equation of State for High-Pressure Phase Equilibria of Mixtures Containing Polymers and Volatile Fluids (Publication 8)

T. Sako, A.H. Wu, and J.M. Prausnitz

Generalized van der Waals theory is used to obtain a three-parameter cubic equation of state applicable to fluids containing small or large molecules, including polymers. The necessary parameters are all obtained from a minimum of experimental information. In extension to mixtures, the equation of state is used to calculate high-pressure phase equilibria for the ethylene-polyethylene system. The relatively simple equation may be useful for engineering-design calculations for fluid mixtures containing polymers, especially when very few experimental data are available.

9. Work in Progress

Efforts are directed at experimental and molecular-thermodynamic studies of (a) phase equilibria for systems containing water, a water-soluble polymer, salt, an organic solvent (e.g., propanol), and carbon dioxide at high pressures, for separation of salts and polymers, (b) liquid-liquid equilibria in two-phase aqueous systems for separation of mixtures of proteins; (c) liquid-liquid equilibria in aqueous mixtures containing salt and an organic solvent that has an upper or lower consolute temperature in the region 10–120°C, for energy efficient, solvent-induced crystallization; (d) phase equilibria for systems forming reverse micelles in dense gases, for

fractionation of polymers and for separation of protein mixtures; (e) molecular simulations for fluids and dilute fluid mixtures in the critical region; (f) phase equilibria for mixtures containing water, heavy hydrocarbons, and hydrogen at high pressures; and (g) enzyme-catalyzed transesterification of triglycerides in dense carbon dioxide.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. D. Dimitrelis and J.M. Prausnitz, "Solubilities of N-Octadecane, Phenanthrene, and Pressures to 60 Bar," *J. Chem. Eng. Data* **34**, 286 (1989); LBL-25528.
2. J.J. de Pablo and J.M. Prausnitz, "Liquid-Liquid Equilibria Including the Critical Region. Transformation to Non-Classical Coordinates," *Fluid Phase Equilib.* **50**, 101 (1990); LBL-25709.
3. A.H. Harvey and J.M. Prausnitz, "Thermodynamics of High-Pressure Aqueous Systems Containing Gases and Salts," *AIChE J.* **35**, 635 (1989); LBL-26001.
4. Y. Liu, A. Harvey, and J.M. Prausnitz, "Thermodynamics of Concentrated Electrolyte Solutions," *Chem. Eng. Commun.* **77**, 43 (1989).
5. G.F. Chou and J.M. Prausnitz, "A Phenomenological Correction to an Equation of State for the Critical Region," *AIChE J.* **35**, 1487 (1989); LBL-26040.
6. S. Michel, H. Hooper, and J.M. Prausnitz, "Mutual Solubilities of Water and Hydrocarbons from an Equation of State. Need for an Unconventional Mixing Rule," *Fluid Phase Equilib.* **45**, 173 (1989); LBL-26379.
7. A.H. Harvey and J.M. Prausnitz, "The Non-Additive Hard Sphere Mixture as a Reference System in Equation of State Calculations," *Fluid Phase Equilib.* **49**, 197 (1989); LBL-25823.
8. T. Sako, A. Wu, and J.M. Prausnitz, "A Cubic Equation of State for High-pressure Phase Equilibrium of Mixtures Containing Polymers and Volatile Fluids," *J. Appl. Poly. Sci.* **38**, 1939 (1989).

LBL Reports

9. D. Dimitrelis and J.M. Prausnitz, "Molecular Thermodynamics of Fluid Mixtures at Low and High Densities," *Chem. Eng. Sci.* (in press); LBL-26794.
10. J.J. de Pablo and J.M. Prausnitz, "Thermodynamics of Liquid-Liquid Equilibria Including the Critical Region: Transformation to Non-Classical Coordinates Using Revised Scaling," accepted by *Fluid Phase Equilib.*; LBL-26147.
11. H.R. Corti, M.W. Krenzer, J.J. de Pablo, and J.M. Prausnitz, "Effect of a Dissolved Gas on the Solubility of an Electrolyte in Aqueous Solution," *IEC Res. Fund.* (in press); LBL-27368.

12. J.J. de Pablo and J.M. Prausnitz, "Phase Equilibria for Fluid Mixtures from Monte-Carlo Simulation," *Fluid Phase Equilib.* (in press); LBL-27721.
13. R. Dohrn, W. Kuenstler, and J.M. Prausnitz, "Correlation of High-Pressure Phase Equilibria in the Retrograde Region with Three Common Equations of State," *Can. J. Chem. Eng.* (in press); LBL-28324.
14. T. Klein and J.M. Prausnitz, "Phase Behavior of Reverse Aqueous Micelles in Compressed Propane at 35°C and Pressures to 30 MPa. Solubilization of Polyethylene Glycol," submitted to *Phys. Chem.*; LBL-28341.
15. M. Krenzer, J.J. de Pablo, and J.M. Prausnitz, "Purification of Aqueous Hydroxyethylcellulose. Extraction of Sodium Acetate with Isopropanol and High-pressure Carbon Dioxide," LBL-28102.
16. J.M. Prausnitz, "Biotechnology: A New Frontier for Molecular Thermodynamics," *Fluid Phase Equilib.* (in press); LBL-27685.
18. J.M. Prausnitz, "Thermodynamic Properties of Hydrogels," AIChE Annual Meeting, Washington, DC, Nov. 1988.
19. J.M. Prausnitz, "Molecular Thermodynamics for Chemical Process Design," Chemical Engineering Department, University of California at Davis, Feb. 1989; Faculty for Chemical Technology, Technical University, Delft, The Netherlands, June 1989; Institute for Thermodynamics, Technical University Berlin, Federal Republic of Germany, June 1989.
20. J.M. Prausnitz, "The Synthetic Character of Molecular Thermodynamics," and "From Apollo to Prometheus: What the Humanities Can Teach Us About Engineering Education," Julian Smith Lectures, Cornell University, Ithaca, NY, Apr. 1989.
21. J.M. Prausnitz, "Molecular Thermodynamics for Biotechnology," Fifth International Conference on Phase Equilibria and Physical Properties in the Chemical Industries, Banff, Alberta, May 1989.
22. J.M. Prausnitz, "Molecular Thermodynamics for Gels and Micelles," Symposium on Applied Chemical Thermodynamics, Utrecht, The Netherlands, June 1989.
23. J.M. Prausnitz, "The Synthetic Character of Molecular Thermodynamics," Chemical Engineering Department and Institute for Petroleum Technology, University of Wyoming, Cheyenne, Sept. 1989.

Invited Talks

17. J.M. Prausnitz, "High-Pressure Vapor-Liquid Equilibria for Aqueous Electrolytes and Gases," AIChE Annual Meeting, Washington, DC, Nov. 1988.

Fossil
Energy

Wastage of Steels in the Erosion-Corrosion (E-C) Environments of Fluidized Bed Combustors*

Alan V. Levy, Investigator

INTRODUCTION

The erosion and erosion-corrosion studies have continued to be primarily directed toward the problem of metal wastage of heat transfer tubes in fluidized bed combustors (FBC), of both bubbling and circulating types. Based upon the understanding of erosion-corrosion metal wastage gained by using actual FBC bed material particles, controlled mixtures of FBC feedstock constituents were prepared in the laboratory and used as erodents to gain a further understanding of the chemical behavior of bed material erodents. The operation of laboratory erosion-corrosion test equipment to simulate the conditions in FBCs necessitated the determination of how test variables such as temperature, particle size, velocity, impact angle, and solids loading affect material wastage at lower particle velocities and temperatures than had been used in previous work. The use of wear resistant thermal spray coatings holds considerable promise to reduce detrimental metal wastage of critical surfaces in FBCs. Their erosion-corrosion behavior was investigated in laboratory tests. The erosion-corrosion behavior of a new type of diffusion coating combining both aluminum and chromium was investigated. Also, the use of thin, ZrO_2 plasma sprayed coatings on the combustion zone surfaces of natural gas combustion engines was investigated. Low Cr content steel alloys with somewhat higher than normal silicon contents were tested at milder test conditions than in earlier work and continued to demonstrate marked reductions in metal wastage. Ongoing and future research will continue in the direction of understanding how and why real materials behave as they do in simulated and real FBC environments. Cooperative efforts with industry increased during the year.

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1. Effect of Test Variables on Erosion-Corrosion (E-C) of Steels Using Bed Material Erodents (Publications 7, 12, and 13)

G.Q. Geng

The erosion-corrosion (E-C) of steels was studied in a laboratory tester at conditions that simulated those in the convection pass region of circulating fluidized bed combustors (CFBCs). The effects of environmental factors such as temperature, particle velocity, impact angle, and erodent feed rate on the E-C metal wastage of the types of steels used in tubular heat exchangers was determined. Using bed materials from actual FBCs as erodents, the behavior of the alloys tested was nearly identical to observed behavior of the same alloys in commercial operating CFBC superheater tube banks. Also, the use of FBC bed materials resulted in behavior that was considerably different from that determined using harder, more inert particles, such as SiO_2 , Al_2O_3 , and SiC. It was determined that low elevated temperatures to $450^\circ C$ caused a minor increase in metal wastage, while increasing the temperature above $450^\circ C$, up to $650^\circ C$, caused a large increase in metal wastage for both 1018 steel and 2.25Cr-1Mo steels. At test temperatures below $450^\circ C$, oxidation *per se* did not play a strong role in the erosion-corrosion of the steels, while it had a much more significant effect at $650^\circ C$.

FBC bed material accumulated on the specimen surfaces at low velocities and protected them against metal wastage. There was a transition velocity, above which the particles no longer accumulated on the surface and the metal wastage markedly increased. The particle velocities that were used in the investigation, 10 and 20 m/sec, which are in the range of those that occur in the convection pass of CFBCs, are generally lower than the transition velocity. Changing the particle impact angle from a shallow angle to a steep angle changed the scale morphology and its behavior. At lower particle velocities the metal wastage at a shallow angle was more than that at a steep angle.

The effect of increasing the erodent feed rate on the E-C behavior of 1018 steel at $450^\circ C$ using sand and CFBC bed material particles was to increase the metal wastage. The effect was found to be related to the oxidation that occurred between particle impacts in micro-sized areas and the amount of interference that occurred between incoming and rebounding particles.

2. Erosion-Corrosion of Thermal Spray Coatings (Publication 19)

B.Q. Wang

The erosion-corrosion (E-C) behavior of several types of protective thermal spray coatings on mild steel was studied to determine the factors that contributed to their erosive wear behavior. They included hard tungsten carbide-cobalt composites and softer, more ductile metals that were designed to provide wear protection. They were E-C tested at the elevated temperature (450°C) using 250- μ m CFBC bed material and quartz particles. The test conditions approximately simulated the E-C environment in the convection pass, superheater region of a CFBC. It was determined that all of the coatings had lower material wastage rates than the base metal, 1018 steel. When the FBC bed material was the erodent, the hardness of the coating had no direct relationship to material wastage: the ductile metal coatings had the same or lower material wastage rates than the harder tungsten carbide-cobalt coatings. When SiO₂, fused quartz particles were used as the erodent, the ratio of the target material hardness to the hardness of the erodent particles appeared to play a significant role in the erosion-corrosion behavior of the thermal spray coatings. The hardness of the coatings had an inverse relationship to material wastage. The erosion material wastage correlated well with the composition and morphology of the coatings. Dense structures, the absence of pores, and the buildup of a protective layer when FBC particles were the erodent resulted in lower material wastage.

The effect of test variables on material wastage of these coatings was also determined. When the test temperature was increased from room temperature to 450°C, the material wastage of the two best performing coatings increased only a small amount. However, the worst performing coating at 450°C had the best performance of the three at room temperature. The material wastage of one coating at room temperature was essentially independent of the erodent particle velocity or impact angle for both impact angles used. However, the other two coatings tested had erosion behavior of typically brittle materials at both test temperatures and both particle velocities, i.e., greater material loss at an impact angle of 90° than at 30°. When the particle velocity was increased from 10 m/sec to 20 m/sec at both test temperatures, the material losses increased. The reasons for the relative behavior of the coatings were determined.

3. The Erosion-Corrosion of Additional Silicon Low Alloy Steels (Publications 3, 11, and 20)

B.Q. Wang

The significant promise of additional silicon, low chromium alloy steels determined in earlier work was pursued to establish the reason for the major decrease that occurred in E-C metal wastage. To determine the role the higher silicon content played, a series of tests was carried out on alloys with additional silicon but no chromium in them, as well as more tests on additional Si, low chromium steels at varying test conditions. It was determined that at test conditions that simulate those in FBCs, the presence of 1.4–1.5% silicon in 2–3% chromium steel, somewhat above its normal silicon content of 0.5% maximum, markedly decreased its E-C metal wastage to even lower rates than occurred on higher chromium, normal silicon content steels. These conditions were considerably milder than those used in earlier tests. So the beneficial effect of the additional silicon was found to be present over a relatively large range of testing conditions. Both of the low carbon steels that contained 2.5–3% silicon and no chromium exhibited lower erosion-corrosion metal wastage rates than even the additional Si, low chromium alloy steels. The precise location of the silicon in the surface layers of the alloy and the mechanism by which it enhances the E-C resistance have still not been determined.

4. SiO₂/Ca Compound Ratio Effects on Erosion-Corrosion of 1018 Steel (Publication 14)

G.Q. Geng

Mixtures of fluidized bed combustor feedstock and bed materials, including SiO₂, CaCO₃, CaO, and CaSO₄, were used as erodents in standard elevated temperature tests to determine the effects of various feedstock constituents on erosivity. Each series of mixtures was made up of SiO₂ and one calcium compound, varying from 100% to 0% SiO₂. It was determined that increasing the ratio of SiO₂ to calcium compound increased the metal wastage. There was a transition ratio of SiO₂/Ca compound where a marked change in metal wastage occurred. On both sides of this ratio, the slopes of the metal loss curves were linear. The slope was very low for the lower SiO₂ content mixtures compared to the higher SiO₂ content mixtures. The transition ratio of SiO₂/CaO decreased as the particle velocity was increased.

Metallographic analysis of tested samples showed that the marked change of metal loss on each side of the transition ratio could be correlated with different characteristics of the scale layer. The transition ratio of SiO_2 to CaCO_3 was related to the formation or lack of formation of a protective layer on the metal surface, while the transition ratio of SiO_2 to CaO or CaSO_4 was related to the formation of a thick, protective layer or a thin, less protective layer on the metal surface. The CaSO_4 and CaO are thought to have acted as a cement to bond a protective layer together on the surface that resulted in lower metal wastage.

5. Use of Thin ZrO_2 Coatings on the Combustion Zone Surfaces of Natural Gas Compression Engines (Publication 16)

A.V. Levy

Thin, $\text{Y}_2\text{O}_3\text{-ZrO}_2$ thermal barrier type coatings used in earlier investigations on the combustion zone surfaces of diesel engines were applied to similar surfaces of the large natural gas fired engines that operate gas compressors in the West Texas gas fields. It was determined that the coatings improved both the performance and the durability of the engines. As a result of the coating, the peak firing pressure was lower and the combustion burn notably improved. Power piston vibration was significantly reduced. The indicated horsepower of the engine was higher, and the engine's operating efficiency increased compared to the same engine operated in the uncoated condition. Fuel consumption was decreased by 10%. Cooling water and oil temperatures were reduced, indicating less heat transfer from the combustion gas through the parts' cross sections to the coolants. Exhaust gas analyses of coated and uncoated engines determined that the coatings resulted in a marked improvement in exhaust emissions.

6. Work in Progress

Behavior of Low Chromium Steels in the Convection Pass of a Circulating Fluidized Bed Combustor (G.Q. Geng)

Two sets of flat specimens of five chromium containing tubing steels were mounted on the shields of superheater tubes in the convection pass of an operating circulating fluidized bed combustor (CFBC) and exposed for 950 and 1855 hours. The type of exposure achieved, directly in the gas-particle flow of the convection pass, had not been done before with controlled thickness specimens.

Precise measurements of thickness losses indicated that the front wall region of the convection pass exposed metal to more severe erosion-corrosion than the rear wall. However, in the case where larger particles were present in the gas because of changing performance in upstream cyclones, the rear wall tube area was more erosive. Being able to use E-C specimens to determine that this major difference in the metal loss was a function of local fluid flow conditions in the CFBC was significant. Generally, the relative behavior of the alloys tested was a function of their chromium content: less metal wastage occurred with higher chromium content. The surface morphology of the E-C specimens exposed in the CFBC was very similar to that observed on laboratory E-C specimens.

Erosion Behavior of Cr-Al Diffusion Coatings (Y. Liu)

A newly developed pack diffusion coating that combines aluminum and chromium in the surface of steel alloys to impart corrosion resistance was investigated to determine its erosion-corrosion behavior compared to that of a straight chromized diffusion coating. The Al-Cr coating had somewhat less material wastage than uncoated base metal specimens or a straight chromized coating. The porous nature of some of the coatings tested contributed to their higher E-C rates, indicating that process control is an important consideration for this type of coating.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. A.V. Levy and Y.F. Man, "Erosion-Corrosion Mechanisms and Rates in Fe-Cr Steels," *WEAR* **131**, 39 (1989).
2. A.V. Levy and Y.F. Man, "Effect of Particle Variables on the Erosion-Corrosion of 9Cr1Mo Steel," *WEAR* **131**, 53 (1989).
3. A.V. Levy and B.Q. Wang, "The Effect of Test Conditions on the Erosion-Corrosion of Alternate Low Alloy Steel Tubing Alloys," *WEAR* **131**, 85 (1989).
4. A.V. Levy, B.Q. Wang, Y.F. Man, and N. Jee, "Erosion-Corrosion of Steels in Simulated and Actual Fluidized Bed Combustor Environments," *WEAR* **131**, 105 (1989).
5. I.M. Hutchings and A.V. Levy, "Thermal Effects in the Erosion of Ductile Metals," *WEAR* **131**, 105 (1989).

Other Publications

6. A.V. Levy, "Mechanism of Combined Erosion Corrosion of Steels at Elevated Temperatures," in *Proc. AIME TMS Symp. Corrosion and Particle Erosion at High Temperatures*, Las Vegas, NV Feb. 1989.

7. G.Q. Geng, B.Q. Wang, and A.V. Levy, "Erosion Behavior of Fluidized Bed Combustor Bed Material Particles," in *Proc. AIME-TMS Symp. Corrosion and Particle Erosion at High Temperatures*, Las Vegas, NV, Feb. 1989.
8. A.V. Levy, "The Abrasion/Erosion and Erosion-Corrosion Characteristics of Steels," in *Proc. ASME Wear of Materials Conf.*, Denver, CO, Apr. 1989, p. 115.
9. A.V. Levy and B.Q. Wang, "Erosion Behavior of Silicon Carbide Fiber-Silicon Carbide Matrix Composites," in *Proc. ASME Wear of Materials Conf.*, Denver, CO, Apr. 1989, p. 129.
10. B.Q. Wang, Z.R. Shui, and A.V. Levy, "Sliding Wear of Chromia Thermal Spray Coatings," in *Proc. ASME Wear of Materials Conf.*, Denver, CO, Apr. 1989, p. 537.
11. A.V. Levy, B.Q. Wang, and G.Q. Geng, "Scale Behavior in Erosion-Corrosion of Low Alloy Steels," NACE Corrosion 89, New Orleans, LA, Apr. 1989, Paper No. 542.
12. A.V. Levy, B.Q. Wang, and G.Q. Geng, "Erosivity of Particles in Circulating Fluidized Bed Combustors," NACE Corrosion 89, New Orleans, LA, Apr. 1989, Paper No. 543.
13. A.V. Levy, B.Q. Wang, and G.Q. Geng, "Characteristics of Erodent Particles in Fluidized Bed Combustors," in *Proc. ASME Int. Conf. Fluidized Bed Combustion*, San Francisco, CA, Apr. 1989, p. 945.
14. A.V. Levy, B.Q. Wang, and G.Q. Geng, "Erosion-Corrosion of Carbon Steel by Particles in Circulating Fluidized Bed Combustors," in *Proc. Second Int. Symp. High Temperature Corrosion*, Les Embiez, France, May 1989.
15. A.V. Levy, "Erosion of Steels by Organic Solvent or Water-Small Solid Particle Slurries," in *Proc. AIME-TMS Symp. Wear-Corrosion Interactions in Liquid Media*, Indianapolis, IN, Oct. 1989.
16. L. Halloman and A.V. Levy, "Ceramic Coated Combustion Zone Components in Natural Gas Compression Engines," ASME Paper No. 90-ICE-26, Energy Technology Conference, New Orleans, LA, Jan. 1990.

Invited Talks

17. A.V. Levy, "Erosion-Corrosion in Power Plant Heat Exchanger Tubing," ASM Golden Gate Materials Technology Conference, Santa Clara, CA, Feb. 1989.
18. B.Q. Wang, G.Q. Geng, and A.V. Levy, "Surface Behavior of Heat Exchanger Tubes in Fluidized Bed Combustors," ICMC Conference, San Diego, CA, Apr. 1989.
19. B.Q. Wang, G.Q. Geng, and A.V. Levy, "Erosion Corrosion of Thermal Spray Coatings for FBC Heat Exchanger Tubes," ASM Materials Week, Indianapolis, IN, Oct. 1989.
20. B.Q. Wang, G.Q. Geng, and A.V. Levy, "Scale Behavior in Erosion-Corrosion of Low Alloy Steels," ASM Materials Week, Indianapolis, IN, Oct. 1989.

Energy
Storage
Systems

ELECTROCHEMICAL ENERGY STORAGE

*Lutgard C. De Jonghe, James W. Evans, Rolf H. Muller, John Newman,
Philip N. Ross, Jr., and Charles W. Tobias, Investigators*

Surface Morphology of Metals in Electrodeposition*

Charles W. Tobias, Investigator

INTRODUCTION

The objective of this project is to gain understanding of the partial processes and their interactions involved in the deposition and dissolution of metals by electrolysis. Of particular interest is the influence of hydrodynamic flow on electrocrystallization, and the distribution of charge-transfer rates on advancing and receding metal profiles, as determined by the electric and concentration fields in the solution, and by the kinetics of the charge-transfer reaction. Control of the morphology of metallic deposits has been traditionally effected by addition agents that interfere with the crystallization process. In energy storage applications, however, other means may have to be employed for the control of morphology.

- Rotating-disk, rotating-cylinder, or planar electrodes in channel-type electrolyzers are used for the preparation of metal deposits on substrates with precisely defined surface topography. The genesis of surface textures is studied, using *in situ* motion-picture microphotography, videorecording, and *post mortem* examination by electron microscopy.

1. The Effect of Convection in Microscopic Grooves on Leveling (Publication 2)

K.S. Jordan and C.W. Tobias

Transport of inhibitors into three types of microscopic branches is evaluated in the presence of Couette and Poiseuille flows. A numerical solution of the Navier-Stokes equations is obtained for various Reynolds numbers and groove geometries. The increase of transport of

inhibitor into v-grooves caused by secondary flows is shown to be negligible when compared to the rate of transport in the stagnant electrolyte. The absence of a major role of microscopic flows on leveling is in contrast to the role such flows may play in enhancing rates of pitting corrosion.

2. Leveling Caused by Inhibitors in Electrodeposition (Publication 3)

K.S. Jordan and C.W. Tobias

The effect of mass transport of an additive on leveling of an angular notch is evaluated. A model is developed to simulate advancing surface contours for the deposition of nickel in the presence of coumarin additive. The model takes into consideration the effect of the Langmuir coefficient and of current density, and employs three different approximations for the mass-transfer boundary layer (see Figure 2-1). Numerical solutions by the boundary-element method yield satisfactory agreement with available experimentally determined profiles. The orientation of microscopic trenches relative to the direction of flow past them is shown to affect the rate of leveling. The existence of an optimum additive flux is demonstrated.

3. Work in Progress

Development of Surface Patterns in Electrodeposition

To develop reliable vehicles for experimental observations, electrode substrates with precisely defined microprofiles were manufactured in the UCB Microelectronics Laboratory. Silicon was chosen as the most suitable material, because of its availability in optically flat form and the ease with which it can be micropatterned. Angular notches of 70°, with depths between 30 and 70 μm , were prepared with excellent geometric definition. Prior to use in electrodeposition studies, thin layers of gold or copper are first vapor-deposited on these profiled silicon surfaces.

The formation of striations in zinc deposited from acid solutions is evaluated using a digital profilometer capable of measuring deposits 1 to 250 μm thick, with minimal distortion. Data are subjected to Fourier analysis and

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Figure 2-1. Advancing profiles in the deposition of nickel in the presence of coumarin. Mass-transfer boundary-layer thickness is $15\ \mu\text{m}$; average current density is $10\ \text{mA}/\text{cm}^2$; standard Watts bath with $0.68\ \mu\text{m}$ coumarin. (A) With mass-transfer boundary layer parallel to planar position of electrode. Flow transverse to trench. (B) With constant mass flux at a great distance, normal to the flat surface. (C) With boundary layer parallel to the electrode surface everywhere. Approximates flow parallel to trench. (XBL 902-438)

correlation techniques to find preferred wavelength and melting characteristics.

The *mechanism of formation of mossy zinc deposits* from alkaline electrolytes is believed to involve

(1) emergence of discrete nodules, leading to an increase in the local overpotential; (2) consequent build-up of OH^- ion concentration and a corresponding shift in the zinc deposition potential; and (3) formation of a needle-like maze of zinc crystals. EDAX spectroscopy reveals no difference in the oxide content of the mossy deposit when compared to the compact zinc layers. Digital profilometry reveals that there is always a sharp increase in surface roughness on the compact zinc layer prior to the initiation of deposition in the mossy form.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. L. McVay, R.H. Muller, and C.W. Tobias, "Application of Videomicroscopy to In-Situ Studies of Electrodeposition," *J. Electrochem. Soc.* **136**, 3384 (1989); LBL-26426.

LBL Reports

2. K.S. Jordan and C.W. Tobias, "The Role of Convection in Electrodeposition into Microscopic Trenches," LBL-28342.
3. K.S. Jordan and C.W. Tobias, "Leveling Caused by Inhibitors; A Theoretical Study," LBL-28343.

Invited Talks

4. R.C. Anderson, R.H. Muller, and C.W. Tobias, "Investigations of Porous Silicon for Vapor Sensing," Fifth International Conference on Solid State Sensors and Actuators, and Eurosensors III, Montreux, Switzerland, June 25-29, 1989, Abstr. No. C-14.4.
5. L. McVay, R.H. Muller, and C.W. Tobias, "Application of Videomicroscopy to In-Situ Studies of Zinc Electrodeposition," Fall Meeting, the Electrochemical Society, Hollywood, FL, Oct. 15-20, 1989; Ext. Abstr. of the *Electrochem. Soc.*, Vol. 89-2, No. 312, 1989; LBL-26426.
6. R.F. Knarr, M. Velasco, S. Lynn, and C.W. Tobias, "Electrochemical Reduction of 2-Ethyl Anthraquinone," AIChE Annual Meeting, San Francisco, CA, Nov. 5-10, 1989, Paper No. 104d.
7. E.W. Egan and J.J.L. Higdon, "Computational Simulation of Buoyancy Driven Flows Using Vortex Methods," 42nd Annual Meeting of the American Physical Society, Division of Fluid Mechanics, Palo Alto, CA, Nov. 10-21, 1989.

Surface Layers on Battery Materials*

Rolf H. Muller, Investigator

INTRODUCTION

The structure, composition, and mode of formation of electrochemical surface layers on electrodes for rechargeable galvanic cells are determined in order to find means to control film properties that result in high power density, cycle life, and energy efficiency. Anodic oxide formation and cathodic metal deposition of interest for battery applications in aqueous media are presently investigated.

Experimental measurements are centered on *in situ* optical techniques sensitive to surface microtopography and composition. Results are employed in theoretical models for the quantitative description of the formation of surface layers.

Studies about the effect of adsorbed materials on the electrocrystallization of metals and the exploration of new means to accelerate electrochemical mass transfer for high-rate metal deposition are reported under "Electrochemical Phase Boundaries," Rolf H. Muller, Investigator.

1. Elastic Light Scattering Measurements During Anodic Film Formation (Publication 4)

S.T. Mayer and R.H. Muller

Angularly resolved light scattering from electrode surfaces during anodic film formation has been used to determine changes in surface microtopography. For the formation of Ag_2O on Ag, the distribution of scattered light changes from one spread over a large range of angles, characteristic of small scattering particles after nucleation, to a distribution near the incident (normal) direction, characteristic of large particles (see Figure 1-1). In contrast, scattering during Cu_2O formation remains distributed over a large range of angles, and scattering centers stay small (see Figure 1-2).

Figure 1-1. Background-subtracted scattering intensity for Ag_2O formation on Ag after application of a potential step from -100 to 290 mV vs Hg/HgO at time zero. Potential held at 290 mV for 160 sec. Each scan required 3.92 sec to acquire and is an average of four individual scans. (XBL 888-2935)

Figure 1-2. Background-subtracted scattering intensity for Cu_2O formation on Cu (111) in 1M KOH after application of a potential step from -600 to -300 mV vs Hg/HgO. Each scan required approximately 8.3 sec to acquire and is an average of ten individual scans. (XBL 897-2856)

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A comparison of scattering measurements from Ag_2O with predictions for a random array of spherical particles of equal size has shown that the observed angular-scattering distribution can only be fitted in the early stages of film formation and requires the use of unrealistically large particle sizes and small changes in number density. The model is therefore at best an approximate representation of the initial oxide film, and its assumptions are not valid after redistribution of the film material. Consequently, scattering measurements have been interpreted by two global quantities, the RMS roughness, derived from the integral of the spectral power density function, and the near-to-far-angle ratio of the spectral power density, which is a measure of particle size. Light-scattering measurements are sensitive to very small changes in RMS roughness (see Figure 1-3).

2. Microtopography of Electrochemical Surface Layers (Publications 5 and 7)

R.H. Muller

Observation of the early stages of anodic and cathodic film formation has been shown to provide information on the mechanisms involved in the process. Spectroscopic ellipsometry, elastic light scattering, Raman spectroscopy, and scanning tunneling microscopy have primarily been used. Ag_2O formation is found to result in a porous dual-layer film structure and involve the redistribution of oxide from small to large growth centers via a dissolved species, which results in a large decrease in the number density of growing nuclei. Cu_2O forms as a single, compact layer that

Figure 1-3. RMS roughness derived from scattering measurements shown in Figure 1-1. (XBL 897-2653B)

remains fine-grained, but a substantial fraction of the oxide is dissolved during film formation. Pb deposition on Ag occurs by repeated nucleation in recessed regions, causing a series of smoothing and roughening cycles.

3. Video Microscopy of Zinc Deposition (Publication 1)

L. McVay, R.H. Muller, and C. W. Tobias

The development of the morphology of zinc deposits during electrolysis from flowing acidic electrolyte has been followed by video microscopy. The evolution of striations in the deposit has been shown to start with a set of randomly distributed protrusions that grow preferentially in the flow direction and coalesce to form ridges (see Figure 3-1).

Figure 3-1. Genesis of a striation in zinc deposition from a set of unaligned protrusions. Flow times shown on figure. 28.5 mA/cm^2 , 3M ZnCl_2 , 3M KCl , $\text{pH} = 1.5$, $\text{Re} = 4000$, $800 \mu\text{m}/\text{image}$. Flow direction from left to right. (XBB 892-1243)

4. Mass Transfer in a Small-Aspect-Ratio Rotating-Disk CVD Reactor (Publication 3)

D.T. Schwartz and R.H. Muller

Mass transfer in a rotating-disk chemical vapor deposition (CVD) reactor has been analyzed theoretically. With the use of a porous injector facing the rotating disk, this system can provide uniform reaction rates over most of the disk surface. Perturbation expansions for the concentration field and the deposition rate for a mass-transfer-limited reaction have been prepared. The perturbation solutions for the effect of injection velocity, substrate rotation rate, and fluid properties compare well with numerical solutions in the literature.

5. Work in Progress

Since many oxide films on battery materials are semiconducting, it is possible that the high-intensity illumination used in Raman spectroscopy modifies electrochemical processes in the films. The effect of high-intensity illumination of copper oxides in alkaline media has been investigated. The cathodic photodecomposition of CuO to form Cu₂O has been observed by Raman spectroscopy and intensity-modulated photocurrent measurements. The reduction of Cu₂O to Cu is also facilitated by illumination.

Structural changes in nickel oxide films are being investigated as a possible cause for the memory effect of nickel electrodes in galvanic cells. Optical properties over the visible spectrum of oxide layers on nickel formed at different potentials have been derived from spectroscopic-ellipsometer measurements. The results are highly reproducible and in good agreement with critically evaluated literature values. New optical models are being developed to represent the transformation between nickel hydroxide and oxyhydroxide.

The formation of rough, nonadherent mossy deposits during zinc deposition from alkaline media, which is detrimental to the cycle life of battery electrodes, is being investigated. The thickness of a compact layer, initially formed before the onset of mossy deposition, has been found to increase with increasing zincate and decreasing KOH concentrations. The compact layer is also thicker at higher current density and fraction of limiting current. Mossy deposits are obtained with saturated or unsaturated

zincate solutions. Surface profiles have shown a sharp increase in surface roughness immediately before moss formation. The oxide content of the mossy deposit does not differ from that of the compact layer.

The formation of zinc oxide films on zinc electrodes in alkaline solutions is being investigated in order to identify the mechanisms by which active and passive films are formed and the effect of electrolyte additives used for the control of shape change.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. L. McVay, R.H. Muller, and C.W. Tobias, "Application of Videomicroscopy to *In Situ* Studies of Electrodeposition," *J. Electrochem. Soc.* **136**, 3384 (1989); LBL-26426.

Other Publications

2. L. McVay, R.H. Muller, and C.W. Tobias, "Application of Video Microscopy to *In Situ* Studies of Zinc Electrodeposition," *Electrochem. Soc.*, Hollywood, FL, Oct. 15-20, 1989, Ext. Abstr. No. 12; LBL-27136.

LBL Reports

3. D.T. Schwartz and R.H. Muller, "Mass Transfer in a Small Aspect Ratio Rotating Disk CVD Reactor," LBL-27882.
4. S.T. Mayer (Ph.D. Thesis), with R.H. Muller, "An *In Situ* Study of the Anodic Film Formation of Cu, Ag and Zn in Alkaline Media," LBL-28085.

Invited Talks

5. R.H. Muller, "Microtopography of Electrochemical Surface Layers," keynote lecture, International Society of Electrochemistry, Kyoto, Japan, Sept. 17-22, 1989; LBL-26742.
6. R.H. Muller, "*In situ* Observation of Anodic and Cathodic Film Growth," International Society of Electrochemistry Post Conference, Advanced *In Situ* Observation of Electrode Surfaces and Electrode Kinetics, Sapporo, Japan, Sept. 25-26, 1989.
7. R.H. Muller, "Advanced Methods to Characterize Electrode Surface Layers," Ninth Battery and Electrochemical Contractors' Conference, Alexandria, VA, Nov. 12-16, 1989; LBL-27700.

Electrode Kinetics and Electrocatalysis*

Philip N. Ross, Investigator

INTRODUCTION

Carbon blacks are important materials used in a variety of battery systems, and each system often makes use of a specific property of the carbon, e.g., conductivity, corrosion resistance, capacitance, catalytic activity, etc. In spite of their importance and wide use, the relation of their chemical properties to precursor and treatment history is not well understood, and considerable advancement in technologies using carbon materials appears possible.

In the case of air electrodes in metal-air batteries, the carbon is used as a support for the active catalyst, i.e., to achieve and maintain high dispersion, and as a current collector, since the active catalyst may not have high bulk conductivity and may be relatively expensive and/or heavy. Thus, the unique properties of carbon of interest in this application are conductivity, surface area, and corrosion resistance. It is known that dramatic changes in structure and chemical properties occur when carbon blacks are heat-treated in an inert atmosphere at temperatures varying from 1000 to 3000°C. Heat-treatment conditions can be combined with selection of the carbon precursor to tailor the properties of the carbon black to suit the application. The particular technical challenge in air electrodes is to develop a carbon with sufficient corrosion resistance, conductivity, and surface area to meet the lifetime and performance requirements for electric-vehicle applications.

A new study was started this year on modified platinum electrocatalysts for the direct oxidation of methanol in acid electrolyte. This study uses modern surface analytical methods [e.g., low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), ion-scattering spectroscopy (ISS)] coupled with electrochemical methods to determine the dependence of catalytic activity on the composition and structure of modified platinum surfaces.

The best known catalysts for the direct oxidation of methanol are platinum surfaces modified by underpotential deposition (UPD) of certain admetals, most especially tin.

The state of the admetal, valence, number and type of ligand, and co-ordination to the platinum surface are all unknown even for the most studied systems like tin. Some studies have speculated that the "active" state of admetal on platinum is an alloy state produced by electrodeposition from the admetal ions in electrolyte; others have suggested the active state is an adsorbed (complexed) ion. We have addressed this question initially by preparing single-crystal surfaces having adatoms in a known chemical state and atomic position, e.g., using ordered Pt₃M alloy surfaces prepared by UHV methods. In the bulk-alloy Pt₃M structure, M atoms are substituted for Pt at the corners of the unit cell. In vacuum, the surfaces of the alloy would ideally have M atoms substituted in an ordered manner for Pt atoms in the surface. It is postulated that the intermetallic bonding in these substitutional positions will stabilize the admetal (M) in these positions in the surface when emersed in electrolyte, and that they will remain in these positions by equilibrium with admetal ions in solution. Study of methanol electro-oxidation kinetics on these ordered surfaces of known composition and structure will enable us to determine the "active" state of the adatom in platinum bimetallic catalysts.

1. CO Chemisorption on [111] and [100] Oriented Single Crystals of the Alloy CoPt₃ (Publication 3)

U. Bardi,[†] B.C. Beard,[‡] and P.N. Ross

In a previous study, it was shown that surfaces of both the [111] and [100] oriented single crystals of CoPt₃ have a "sandwich" structure with an outermost atomic layer that is essentially pure Pt and a second layer enriched in Co (with respect to the bulk). In the present work, we report a study of the energetics of carbon monoxide chemisorption on these surfaces, and compare the results with our previous study of carbon monoxide adsorption on Pt₃Ti surfaces. A surprising similarity in the activation energy for desorption of carbon monoxide from Pt sites on both the CoPt₃ and Pt₃Ti surfaces was found, with the adsorption energy being substantially lower on the alloy surfaces than for pure Pt surfaces of the same orientation (see Figure 1-1). Since the CoPt₃ surfaces have a pure Pt top layer, it appears that the intermetallic bonding between Co in the second layer and Pt in the top layer changes the electronic states available for the bonding of carbon monoxide to the surface.

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Figure 1-1. Carbon monoxide thermal-desorption spectra after 10-Langmuir exposure: at 300 K from the [100] surfaces of pure Pt (1') and Pt₃Co (2'); at 250 K from the [111] surfaces of pure Pt (1) and Pt₃Co(2). Heating rate: 15 K/sec in all cases. (XBL 902-5738)

2. The Structure and Activity of Pt-Co Alloys as Oxygen-Reduction Electrocatalysts (Publication 4)

B.C. Beard[†] and P.N. Ross, Jr.

Carbon-supported Pt-Co (3:1 atom ratio) catalysts were prepared in both acid and alkaline aqueous media, followed by heat treatments to promote alloy formation. Both preparations began with a commercial 10% Pt-on-carbon catalyst with Pt particle sizes of 15–30 Å. Significantly greater alloying was observed in the catalyst prepared in the acid medium. X-ray diffraction studies of the acid-prepared catalyst demonstrated lattice parameters tending away from Pt (3.927 Å) and toward that for Pt₃Co (3.831 Å), greatly increased particle sizes, and significant ordering evidenced by the presence of superlattice reflections. In all cases, catalysts prepared in the alkaline medium were alloyed to a lesser extent, were of moderately increased particle size, and gave no identification of alloy ordering. Activity testing under phosphoric acid fuel-cell conditions demonstrated that the most highly alloyed catalysts were not significantly more active than pure Pt catalyst of comparable crystallite size. Loss of cobalt in the phosphoric acid environment was the lowest in catalysts that were the most alloyed, and where the Pt₃Co ordered phase was present.

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3. The Surface Structure and Composition of $\langle 111 \rangle$, $\langle 100 \rangle$, and $\langle 110 \rangle$ Oriented Single Crystals of the Ordered Alloy Pt₃Sn (Publication 5)

A.N. Haner and P.N. Ross

The surface composition and structure of $\langle 111 \rangle$, $\langle 100 \rangle$, and $\langle 110 \rangle$ oriented crystals of the ordered alloy Pt₃Sn (L1₂ or Cu₃Au type) were studied by a combination of techniques, including AES, angle-resolved photoelectron spectroscopy (ARXPS), and low-energy ion-scattering spectroscopy (LEISS). As anticipated by the classical theory of surface segregation by van Santen and Sachtler, the $\langle 111 \rangle$ surface had the ideal bulk termination structure, which has the same composition as the bulk, and the surface of the $\langle 100 \rangle$ crystal was Sn-enriched relative to the bulk. However, the $\langle 100 \rangle$ crystal is best described as a preferential termination of the bulk crystal in (100) planes, by the formation of a step-terrace structure having (100) terraces connected by diatomic steps, which is not a structure anticipated in the theory. The $\langle 110 \rangle$ crystal has a reconstructed surface region at least three atomic layers deep, with a structure possibly related to that of the ordered PtSn alloy (B8₁ or NiAs type) (see Figure 3-1). Adsorption of oxygen at low pressure (10⁻⁷ torr) results in oxygen bonded preferentially to Sn atoms, one oxygen on every other Sn atom at these conditions. The oxygen desorbs from the Pt₃Sn surfaces at a temperature ~200 K higher than from pure Pt surfaces. These results suggest possibly interesting properties for this alloy as a catalyst for partial oxidation reactions.

4. Work in Progress

A study of the kinetics of methanol oxidation on Pt₃Sn is nearing completion. Even though this alloy has a very exothermic heat of mixing, surface enrichment of Sn occurs

Figure 3-1. (a) Schematic of LEED pattern from a clean annealed [110] single crystal of Pt₃Sn; O—fundamental beams for fcc (110)—1 × 1; X—superlattice beams; (b) possible real-space structure of surface based on the LEED pattern. (XBL 902-450)

on two of the three low-index faces, (100) and (110). The (110) surface actually reconstructs in the first few atomic layers to form a distorted form of the hexagonal structure of the ordered stoichiometric alloy Pt₃Sn. The surface composition of these two faces appears to be 50% Sn, versus 25% in the bulk. Neither methanol nor even carbon monoxide (!) is adsorbed from the gas phase onto the Pt₃Sn surface at room temperature. The voltammetry indicated that there was no hydrogen adsorption on the Pt₃Sn surface in acid electrolyte, and the surface was a very poor catalyst for methanol oxidation. Two properties of this material appear to be causing the low activity: (1) strong intermetallic bonding and rehybridization reduces the number of Pt d-electrons available for bonding to adsorbates; (2) the concentration of Sn in the surface is too high, since a critical ensemble of Pt-Pt sites appears to be required for effective catalysis.

A dilute alloy of Sn in Pt (e.g., 5%) has been prepared and will be examined in our UHV system for its equilibrium surface composition. The intent is to determine whether the surface composition of Pt-Sn alloys can be controlled by manipulating the bulk composition.

The study of methanol-oxidation kinetics on Pt surfaces modified by electrodeposited Sn is still in progress. On a polycrystalline Pt sample, a three-to-five-fold acceleration of the rate of methanol oxidation in sulfuric acid was observed; but on the Pt low-index single-crystal surfaces, only the (111) surface showed enhanced catalysis in the presence of Sn. Thus there appears to be a very surprising effect of surface structure on the catalytic effect of the adsorbed Sn. It is not clear what causes this effect; possibly a different state of Sn results from adsorption on the different Pt faces.

A series of experiments to understand the effect of the Pt surface structure on the catalytic action of Sn on methanol oxidation is in progress. The first is to vary the surface coverage of Sn on each surface by changing the concentration of Sn in the electrolyte (there is a different adsorption isotherm for Sn on each crystal face of Pt), then comparing activity vs coverage. If the activity for a given coverage is different on the different surfaces, then photoelectron spectroscopy will be used to determine whether the chemical state of the Sn is different on different surfaces at the same coverage.

Recent testing of air electrodes fabricated with the tailored corrosion-resistant carbons has shown that these electrodes suffer from excessive polarization at high current density. The problem appears to be the intrinsic nonwettability of the highly graphitized corrosion-resistant

carbon, particularly when it is mixed with the Teflon binder. Two separate approaches will be used to address this problem. One is to find a surface treatment that increases the wettability of the carbon without affecting its corrosion resistance. One surface treatment that will be tried is attachment of aromatic carboxylic acids, since the phenyl groups should attach to the basal plane, and the oxygen group should increase the interaction with water, producing increased wetting of the basal plane. The second is to attach aromatic quinones to the carbon surface in sufficient number so as to produce sufficient surface concentration of oxygen to cause a nonwetting-to-wetting transition. An auxiliary benefit of these surface modifications may be that these functional groups may have redox properties with sufficiently high pseudo-capacitance to satisfy the peak current requirements in a vehicle (short acceleration but not hill climbing). Again, aromatic carboxylic acids may perform this function as well, or aromatic quinones.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. N. Staud, H. Sokol, and P.N. Ross, "The Corrosion of Carbon Black Anodes in Alkaline Electrolyte: IV. Current Efficiencies for Oxygen Evolution of Metal Oxide Impregnated Graphitized Furnace Blacks," *J. Electrochem. Soc.* **136**, 357 (1989); LBL-26927.

Other Publications

2. P.N. Ross, "Zinc Electrode and Rechargeable Zinc-Air Battery," U.S. Patent Number 4,842,963, June 27, 1989.

LBL Reports

3. U. Bardi, B.C. Beard, and P.N. Ross, "CO Chemisorption on [111] and [100] Oriented Single Crystals of the Alloy CoPt," *J. Catal.* (in press); LBL-27538.
4. B.C. Beard and P.N. Ross, Jr., "The Structure and Activity of Pt-Co Alloys as Oxygen Reduction Electrocatalysts," submitted to *J. Electrochem. Soc.*; LBL-28663.
5. A.N. Haner and P.N. Ross, "The Surface Structure and Composition of {111}, {100}, and {110} Oriented Single Crystals of the Ordered Alloy Pt₃Sn," submitted to *Surf. Sci.*; LBL-28074.

Electrical and Electrochemical Behavior of Particulate Electrodes*

J.W. Evans, Investigator

INTRODUCTION

The electrochemical behavior of a zinc-air cell equipped with a particulate zinc electrode is being examined. On a laboratory scale the cell has shown performance that on scale-up should result in a battery exceeding DOE specifications for an electric van. The zinc (or zinc-coated) particles form a stationary bed, and electrolyte flow through this electrode is by solutal natural convection. The air electrode is a commercially available monofunctional one.

1. A Zinc-Air Cell Employing a Packed-Bed Anode (Publication 1)

J.W. Evans and G. Savaskan

A cell with a particulate zinc electrode and a monofunctional air electrode has been studied on a laboratory scale. The cell has the feature of relying on solutal natural convection, rather than a pump, for electrolyte circulation. Cells of 80 cm² and 400 cm² (air electrode area) have been discharged at constant or stepped current. Power density is plotted versus current density for the smaller cell in Figure 1-1 at two depths of discharge. A peak power is achieved at a current density of approximately 148 mA/cm². In two cases cell discharge was halted and restarted after many hours with little or no impact on cell voltage. Based on the laboratory data, a

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Figure 1-1. Power versus current density at 20% and 40% DOD. (XBL 902-514)

preliminary design of a 32-kWh battery was completed. The projected specific energy of this cell is 177 Wh/kg, while the peak specific power is 238 W/kg (20% depth of discharge), well in excess of Department of Energy targets for a battery for an electric van.

2. Work in Progress

Experiments are being carried out to obtain further information on the behavior of the zinc-air cell with the packed-bed anode. Amongst these are determinations of the rate of self-discharge and of the performance of the cell during various discharge "protocols" (for example, constant power).

1989 PUBLICATIONS AND REPORTS

LBL Reports

1. J.W. Evans and G. Savaskan, "A Zinc-Air Cell Employing a Packed Bed Anode," LBL-28290.

Electrochemical Properties of Solid Electrolytes*

Lutgard C. De Jonghe, Investigator

INTRODUCTION

The mission of the current research program is the realization of high-performance secondary batteries through advances in both solid electrolyte and novel electrode research. Advances in materials exhibiting high levels of ionic conduction in the solid state have led to worldwide efforts in the development of all-solid-state rechargeable batteries. Although higher current densities are achievable with liquid electrolytes, all-solid-state cells offer inherent advantages of negligible self-discharge, long cycle life, high reliability, and virtual absence of container corrosion. Elegant work on polycrystalline and vitreous electrolytes has led to solid electrolytes with suitable ionic conductivities for battery development. However, the superior mechanical properties of elastomeric electrolytes, combined with the simplicity of fabrication of thin separator films from these materials, has led to very active pursuit of solid-state cells based on solid polymer electrolytes (SPEs). Although solid polymer electrolytes generally have lower ionic conductivities than their polycrystalline and vitreous counterparts, the simplicity of casting thin films (10 to 100 μm) from dilute solutions compensates somewhat for this limitation. While many polymeric electrolytes have been described in the literature, the best known SPE is undoubtedly polyethylene oxide (PEO) complexed with an appropriate electrolyte salt. The operating temperature of SPE cells generally falls in the range of ambient to 100°C, with the highest levels of performance occurring in the elevated-temperature regime, with claims of performance that meet the demands of electric vehicle application. Initial efforts toward ambient-temperature operation of such cells were not promising due to the rapid decrease in ionic conductivity below about 60°C. However, further investigation into the nature of ionic conductivity in polymeric electrolytes has led to the conclusion that ion transport is strictly through the amorphous regions of these polymers, which tend to crystallize with decreasing temperature. By lowering the glass transition temperature of the polymer electrolyte, either by structural modification or by addition of

plasticizing electrolyte salts, sufficiently high conductivities for ambient-temperature operation can be achieved. Reported results for a number of such cells have indicated that high-performance solid-state batteries are nearing commercialization. To date, the majority of these advanced lithium SPE batteries have utilized positive electrodes based on intercalation chemistry. However, work in this laboratory has led to the development of a novel class of solid-state, organic positive electrodes that not only operate on an entirely new principle for energy storage but also have demonstrated performances in a number of instances exceeding those for intercalation electrodes in solid-state lithium and sodium batteries. The electrical, physical, and chemical properties of this novel class of solid redox polymerization electrodes are studied as potential candidates for high-energy-density, high-power-density batteries. Solid-state laboratory cells having alkali metal anodes (i.e., Na, K), solid polymer electrolytes, and polydisulfide polymerization electrodes are fabricated and evaluated in terms of specific energy and power, cycle life, and temperature dependence of cell performance. Investigations of electrodes and electrolytes in functioning cells provide information of interfacial phenomena and identify processes that are limiting to the performance of these advanced batteries. *In situ* dc techniques are used on complete cells to determine bulk and interfacial properties and their relative importance in controlling battery polarization as a function of current density, state of charge, and temperature. Fundamental studies of solid polymer electrolytes are also coupled with in-cell data in an effort to optimize battery performance.

1. Electrode Kinetics of Organodisulfide Cathodes for Storage Batteries (Publication 8)

M. Liu, S.J. Visco, and L.C. De Jonghe

The electrode kinetics of a diverse group of organodisulfide cathode materials were systematically investigated. The electrochemical behavior of these redox couples was studied as a function of the organic moiety (R) in the organodisulfide species (RSSR). These studies were performed with a variety of working electrodes, including platinum, glassy carbon, graphite, stainless steel, aluminum, and copper. The possible reaction pathways and corresponding mechanisms were hypothetically proposed, theoretically analyzed, and experimentally verified. Reaction orders for various organodisulfides and the corresponding thiolate anions were determined from the dependence of the current at a rotating-disk electrode (RDE) with rotation speed at constant electrode potential without varying the bulk concentration (since the effective concentration of electroactive species at the surface of an

*This work was supported by the Assistant Secretary of Conservation and Renewable Energy, Office of Energy Storage and Distribution, Energy Storage Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

RDE is a function of rotation speed). Exchange currents, transfer coefficients, and stoichiometric coefficients were determined from polarization measurements at either stationary electrodes or RDEs under experimental constraints that ensured that the electrochemical processes were completely controlled by electrode kinetics. Observations showed that while electron-transfer rate constants varied with organic moiety, the mechanistic details of the redox path were invariant with the R groups of the organodisulfide compounds (RSSR). The reaction mechanism, as determined from experimental observations, can be expressed as

for the oxidation of thiolate anions (RS^-) to the corresponding organodisulfides. The first step in the redox mechanism, charge transfer, is rate limiting, while the second step, chemical reaction, is at equilibrium. The observed transfer coefficients are quite asymmetric and vary as a function of the R group in RSSR and the electrode material. The standard rate constants are also affected by the nature of the organic moiety R and are in the range of 10^{-8} to 10^{-6} from ambient to 100°C . Further, and in particular, electrode kinetics were enhanced by the addition of several electrocatalysts, as shown by electroanalytical techniques, and by the polarization behavior of Na/β -alumina/RSSR cells.

2. Electrochemical Investigations of a Class of Novel Redox Cathodes (Publication 6)

M. Liu, S.J. Visco, and L.C. De Jonghe

A new class of polymeric positive electrode materials that operate on a novel principle for energy storage has been introduced in this laboratory. The polymeric materials have been named solid redox polymerization electrodes (SRPEs) due to the reversible polymerization/depolymerization reaction that occurs on charge/discharge of the electrode (see Figure 2-1). SRPEs are easy to synthesize, are air stable, and should be very inexpensive in bulk quantities. The polymerization electrodes are a broad class of materials that not only have low equivalent weights but also are inherently reversible to most metal ions, allowing for the fabrication of solid-state cells having a variety of metal anodes. The cell reaction for SRPE-based cells can be described for a simple case as

Figure 2-1. Formation of intermolecular S-S bridges during protein folding, and the related process of electropolymerization/depolymerization. (XBL 901-97)

where M is an alkali metal (Li, Na, K) and R is an organic group. In the broader sense, SRPEs can have more than two S groups per monomer R unit and are reversible to other monovalent and divalent metals. As one can see from the above reaction scheme, in the fully charged state the SRPE electrode consists of a polydisulfide polymer that is depolymerized on discharge by scission of sulfur-sulfur bonds, leading to the formation of dithiolate salts in the fully discharged cell. The cells tested to date include both solid-state lithium and sodium cells, with theoretical energy densities in the range of 90 to 1,500 Wh/kg, as shown in Table 2-1.

Composite SRPEs consisting of polydisulfide polymers, polyethylene oxide (electrolyte), and dispersed carbon black were cycled in various cells, including $\text{Na}(\text{liq.})/\beta$ /SRPE, $\text{Na}(\text{solid})/\text{PEO}/\text{SRPE}$, and $\text{Li}(\text{solid})/\text{PEO}/\text{SRPE}$. Na/β /SRPE cells clearly demonstrated the reversibility of solid-state polydisulfide electrodes to sodium. The sodium cells were cycled at 130 to 140°C at the 1.2c rate ($2.0 \text{ mA}/\text{cm}^2$) for 40 to 50 cycles (80% of capacity) with no discernible deterioration with cycling. Na/β /SRPE cells also demonstrated rate capabilities of up to 6c rate ($10 \text{ mA}/\text{cm}^2$) with close to 100% utilization of capacity and no evidence of adverse effects on electrode integrity, even under situations of abusive polarization on discharge or charge. Solid-state $\text{Na}/\text{PEO}/\text{SRPE}$ and $\text{Na}_{3.75}\text{Pb}/\text{PEO}/\text{SRPE}$ cells were also successfully cycled, attaining the highest current densities yet reported for solid-state sodium cells. However, computer-driven four-probe dc techniques developed in this laboratory for isolating the various contributions to cell polarization show evidence for reaction of the sodium electrode with the polyethylene oxide solid electrolyte. This is not observed with lithium

TABLE 2-1: EQUIVALENT WEIGHTS AND THEORETICAL ENERGY DENSITIES OF REPRESENTATIVE (SRS) _n COMPOUNDS				
MONOMER	Equivalent Weight	Energy Density (Wh/kg) Li/(SRS) _n (OCV = 3.0V)	Energy Density (Wh/kg) Na/(SRS) _n (OCV = 2.7V)	POLYMER NOMENCLATURE
$\text{SCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{S}$	76	870 (OCV = 2.7 V)	600 (OCV = 2.2 V)	X0
74	990	750	X1
58	1240	890	X5
74	990	750	X6
TiS ₂	112	560 (OCV = 2.5 V)		

electrodes and may be due to the higher sensitivity of sodium metal to impurities in the electrolyte, such as water, solvent, etc.

3. All-Solid-State, Thin-Film Rechargeable Lithium Batteries with Novel Redox Cathodes (Publication 5)

M. Liu, S.J. Visco, and L.C. De Jonghe

The dramatic proliferation of devices based on semiconductor technology is a strong testament to the predictability and reliability of solid-state technology. In a similar vein, advances in materials exhibiting high levels of ionic conduction in the solid state have led to worldwide efforts in the development of high-performance, all-solid-state rechargeable batteries. Many of these advanced batteries have utilized lithium negative electrodes,

intercalation compounds such as TiS₂ or V₆O₁₃ as the positive electrode, and solid polymeric electrolytes such as polyethylene oxide (PEO) as the separator. Efforts in this laboratory have led to the development of novel positive electrodes for use in solid-state batteries that operate on an entirely new principle for energy storage, and that outperform intercalation-based electrodes. The new materials are a broad class of polyorganodisulfides and are named solid redox polymerization electrodes (SRPEs).

Various solid redox polymerization electrodes were tested in solid-state batteries of the type M/PEO/SRPE, where M is an alkali metal anode (Li, Na, K). All-solid-state batteries having lithium anodes have demonstrated the highest levels of performance to date for this system. One of the Li/PEO/SRPE cells has achieved 350 cycles in the temperature range of 50°C to 90°C with a sustained energy density of 260 Wh/kg (240 Wh/l), power density of 160 W/kg (140 W/l), and up to 89% of cathode utilization at

90% voltage efficiency. At 100°C, power densities of over 2400 W/kg at an energy density of 200 Wh/kg have been achieved with up to 96% utilization of cathode capacity. Furthermore, four-probe dc techniques show the Li/PEO and PEO/SRPE interfaces to be stable and essentially invariant with cycling.

The densities of one of the SRPE polymers and its dilithium salt were measured by volumetric displacement. The density of the X1 polymer (see Table 2-1) was determined to be 1.8 g/cm³, and its corresponding salt was found to be 1.6 g/cm³. Accordingly, the volumetric and gravimetric capacities of composite films based on X1, PEO, and carbon black were calculated based on physical mixing of each component as a function of weight percent of active material in the composite electrode. (The true values may be somewhat higher due to miscibility of X1 in PEO.) The same calculations were performed for a representative intercalation electrode, TiS₂, for comparison. The results of these calculations are shown in Table 3-1. The film capacities can then be used to calculate the thickness of the SRPE electrode as a function of surface

capacity and load level, as shown in Table 3-2. (SRPE electrodes were generally loaded between 30 and 60 wt%.) As can be seen from Table 3-2, a composite SRPE electrode loaded with 30 wt% X1 with a surface capacity of 3 C/cm² would have a thickness of about 60 µm. If a cell is constructed with the above positive electrode and a 4:1 excess of lithium (16 µm), the total cell thickness, including 10 µm for current collectors, would be less than 100 µm. The rate capacity and capacity utilization for solid-state cells based on SRPE materials is quite encouraging for eventual commercialization of these materials. In fact, the performance of Li/PEO/SRPE single cells meets the demands of electric vehicle and/or load-leveling applications.

4. Work in Progress

Cycle testing of alkali metal/polydisulfide cells is continuing, with emphasis on scale-up of Li/PEO/SRPE cell surface area/capacity. The majority of composite

TABLE 3-1: FILM CAPACITIES FOR COMPOSITE POSITIVE ELECTRODES HAVING VARIABLE LOAD OF ACTIVE MATERIAL, 7 WT% CARBON, AND BALANCE PEO						
Active Material	Loading Level	Density	Volumetric Capacity Density	Gravimetric Capacity Density	Volumetric* Energy Density (vs. Li)	Gravimetric* Energy Density (vs. Li)
	Weight Percent	g/cm ³	Ah/cm ³	Ah/g	Wh/cm ³	Wh/g
X1	100	1.8	0.67	0.36	2.01	1.08
	50	1.5	0.25	0.168	0.75	0.504
	30	1.4	0.15	0.11	0.45	0.33
TiS ₂	100	3.2	0.77	0.22	1.93	0.55
	50	1.77	0.18	0.10	0.46	0.25
	30	1.56	0.10	0.066	0.25	0.165
Lithium	100	0.534	2.0	3.8		

*Volumetric and gravimetric energy densities calculated by multiplying the corresponding capacity densities by the estimated OCV vs. a lithium negative electrode (X1: 3.0 volts, TiS₂: 2.5 volts)

TABLE 3-2: FILM THICKNESS AND WEIGHT AS A FUNCTION OF LOADING			
Active Material	Loading Level Weight Percent	Surface Capacity: 6 C/cm ²	
		Thickness μm	Weight mg/cm ²
X1	100	25	4.5
	50	67	10
	30	110	15.6
Lithium	100	8	0.45

cathodes tested are based on one of two polydisulfide polymers, those derived from dimercapto dithiazole or trithiocyanuric acid, as these materials have exhibited the highest levels of performance and reliability to date. Four-probe dc techniques are also used to observe cell performance *in situ* as a function of temperature, and thereby determine the activation energy for polarization of the Li/PEO interface, conduction in the PEO solid electrolyte, and polarization of the composite SRPE. AC impedance studies are used to complement four-probe dc measurements in the determination of interfacial resistivities, electrolyte conductivities, and measurement of exchange current densities for SRPE composites. Cathode utilization in Li/PEO/SRPE, Na/PEO/SRPE, and Na/β"/SRPE cells are investigated as a function of loading of active material in the composite cathode, current density, art of fabrication, and temperature, in order to ascertain optimum loading levels for scale-up cells. In a similar vein, random and/or block copolymers of various multithio acids, $-(SRS)_n-(SR'S)_x-$, are examined in an effort to further reduce the equivalent weight of SRPE materials whole boosting the performance of the electrodes.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. S.J. Visco, C.C. Mailhe, L.C. De Jonghe, and M.B. Armand, "A Novel Class of Organosulfur Electrodes for Energy

Storage," J. Electrochem. Soc. **136**, 661 (1989); LBL-23598.

2. M. Liu, S.J. Visco, and L.C. De Jonghe, "Electrochemical Properties of Organic Disulfide/Thiolate Redox Couples," J. Electrochem. Soc. **136**, 2571 (1989); LBL-25638.
3. S.J. Visco and J.C. De Jonghe, "Sodium/Beta"-alumina Batteries Operating at Intermediate Temperatures," Mat. Res. Soc. Symp. Proc. **135**, 553 (1989); LBL-26061.

Other Publications

4. S.J. Visco, M. Liu, and L.C. De Jonghe, "Ambient-Temperature High-Rate Lithium/Organosulfur Batteries," in *Proc. 176th Meeting of the Electrochemical Society*, Hollywood, FL, Oct. 15-20, 1989, Ext. Abs. No. 60.
5. M. Liu, S.J. Visco, and L.C. De Jonghe, "All-Solid State, Thin-Film, Rechargeable Lithium Batteries with Novel Solid Redox Cathodes," in *Proc. 176th Meeting of the Electrochemical Society*, Hollywood, FL, Oct. 15-20, 1989, Ext. Abs. No. 65; LBL-27964.
6. M. Liu, S.J. Visco, and L.C. De Jonghe, "Electrochemical Investigations of a Class of Novel Redox Cathodes," in *Proc. 176th Meeting of the Electrochemical Society*, Hollywood, FL, Oct. 15-20, 1989, Ext. Abs. No. 66; LBL-27963.
7. S.J. Visco, M. Liu, M.B. Armand, and L.C. De Jonghe, "Novel High-Rate, Solid-State Lithium Batteries and Their Relationship to Protein Folding," in *Proc. 176th Meeting of the Electrochemical Society*, Hollywood, FL, Oct. 15-20, 1989, Ext. Abs. No. 70.

LBL Reports

8. M. Liu, S.J. Visco, and L.C. De Jonghe, "Electrode Kinetics of Organodisulfide Cathodes for Storage Batteries," LBL-24906.

Invited Talks

9. S.J. Visco, M. Liu, M.B. Armand, and L.C. De Jonghe, "Novel, High-Rate, All Solid-State, Sodium and

Lithium/Organosulfur Batteries," Battery and Electrochemical Contractor's Conference, Alexandria, VA, Nov. 12-16, 1989; LBL-27593.

10. S.J. Visco, M. Liu, P. Kimes, and L.C. De Jonghe, "Properties and Morphology of Doped Polycrystalline Beta"-Alumina Electrolytes," Battery and Electrochemical Contractor's Conference, Alexandria, VA, Nov. 12-16, 1989; LBL-27585.

Analysis and Simulation of Electrochemical Systems*

John Newman, Investigator

INTRODUCTION

This program involves fundamental investigations of the transport and interfacial phenomena important in electrochemical systems. Results of this work are used to analyze experimental data, to identify important system parameters, and to aid in the design and scale-up of electrochemical systems. Specific projects include the analysis of transient and steady-state transport processes in solid polymer electrolytes, mathematical modeling of the Li-Al/FeS₂ and Na/FeCl₂ batteries, theoretical investigations of inductance effects in high-power batteries, an investigation of the ac impedance behavior of porous electrodes, mathematical modeling of current distributions and its extension into corrosion protection, an experimental investigation of the conductivity of sodium polysulfide melts at various conditions, and the rigorous interpretation of cyclic voltammetry and ac impedance experiments.

1. Corrections to Kinetic Measurements Taken on a Disk Electrode (Publication 1)

A.C. West and J. Newman

Below the limiting current, the rotating-disk electrode has a nonuniform current distribution. When the nonuniformities are not explicitly accounted for, errors in values of kinetic parameters determined through measurements on a disk can result. In this analysis, valid for Tafel kinetics, correction factors are obtained as a function of the dimensionless average current density. It is assumed that ohmic corrections are made by the interruption of current. The results indicate that, under certain conditions, the errors are negligible and that the disk geometry, despite its nonuniformities, is adequate for the investigation of systems characterized by Tafel kinetics.

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2. Mathematical Modeling of the Sodium/Iron Chloride Battery (Publication 14)

M. Sudoh and J. Newman

A mathematical model of the sodium/iron chloride battery containing a molten AlCl₃-NaCl electrolyte is presented. A cylindrical cell consisting of a positive iron electrode, an electrolyte reservoir, a separator, and a negative sodium electrode is considered. The analysis uses concentrated-solution theory within the framework of a macroscopic porous-electrode model. The effects of the state of discharge, the cell temperature, the precipitation and dissolution rates of NaCl, and the current density on the current-potential relation during the discharge and charge cycles are discussed. The major influences on battery performance are changes in porosity and component volume fractions during cycling.

3. A Criterion to Verify Current-Distribution Calculations (Publication 16)

A.C. West, J.H. Sukamoto, and J. Newman

Practical uses of the results of the singular-perturbation analysis given by West and Newman¹ of the current distribution near an electrode edge as a primary distribution is approached are demonstrated. These results are applicable for a large, finite ohmic resistance as compared to the resistance of interfacial, faradaic reaction. By applying the analysis to a slotted-electrode cell, it is shown how the results can be used to verify the accuracy of numerical results obtained for a specific geometry. The established criterion is valid for the conditions where calculations are most likely to be in error.

1. A.C. West and J. Newman, *J. Electrochem. Soc.* **136**, 2391 (1989); LBL-26153.

4. Effects of Finite Rates of a Homogeneous Reaction on the Steady-State Dissolution of Copper in Chloride Solutions (Publication 6)

A.K. Hauser and J. Newman

The steady-state dissolution of a copper rotating disk in 0.1N HCl is investigated. Specifically, the effect of finite rates of the homogeneous complexing reaction is explored by utilizing a perturbation analysis. Formulating the singular perturbation problem leads to a better understanding of the physical nature of the system and enables one to characterize quantitatively the numerical

errors resulting from the Stefan-Maxwell algorithm that arise for certain values of the rate constants. Additionally, a new way of plotting the steady-state polarization behavior is introduced that reduces the number of independent parameters of the system to a minimum. Concentration and potential profiles as functions of distance from the electrode, calculated using a macroscopic model based on concentrated-solution theory and the Butler-Volmer kinetics, are interpreted by means of the perturbation analysis.

5. Interpretation of Kinetic Rate Data Taken in a Channel Flow Cell (Publication 9)

A.C. West and J. Newman

Nonuniform current distributions can complicate the interpretation of kinetic rate measurements. This paper shows explicitly how nonuniformities affect measurements in the flow-channel cell. Results are given for linear and Tafel kinetics and can be used to relate measurable electrochemical quantities to kinetic parameters. In addition to the appropriate polarization parameter, the interpretation of data requires knowledge of the ratio of the two characteristic lengths and the placement of the reference electrode. The analysis assumes that the ohmic potential drop is subtracted from the measurements by the interruption of the current and that the concentration variations are negligible.

6. Differential Diffusion Coefficients of Sodium Polysulfide Melts (Publication 8)

S.D. Thompson and J. Newman

The method of restricted diffusion has been applied to sodium polysulfide melts in order to determine differential diffusion coefficients spanning the composition range of the single-phase liquid region (Na_2S_3 to Na_2S_5), at temperatures between 300 and 350°C. Molybdenum electrodes at the ends of the cell gave open-circuit potentials in response to the transient concentration difference. The shape of the potential vs time plots showed the expected dependence on the initial concentration profile. The following expression summarizes the experimental data:

$$D = 0.0153 \exp(-5890/T) \exp(5.30x_c) \text{ cm}^2/\text{sec}$$

The diffusion coefficients showed a temperature dependence in harmony with viscosity data, but not with conductivity data.

7. Work in Progress

A model that will permit the quantitative interpretation of experimental observations of solid polymer electrolytes is being developed. More specifically, the model will help in determining fundamental transport properties from transient and steady-state experiments. The effects of membrane water content and temperature on these properties will be elucidated. The three-phase region at the membrane-electrode interface will also be included.

A model that uses Duhamel's theorem to simulate cyclic voltammetry experiments at stationary and rotating-disk electrodes is being improved. The model can account for mass-transfer effects, faradaic reactions, and adsorption phenomena, which will permit the quantitative interpretation of data. In particular, it is being used to study linear-sweep voltammograms of the reduction of nitrate in acidic nickel solutions.

Inductance effects associated with the discharge of high-power batteries are being investigated. Results from simplified and highly idealized systems have provided insight into how a realistic model should be developed. Emphasis is placed on identifying the proper scale-up parameters and the optimum configuration for a high-power battery as well as its proper positioning within the circuit.

Previous work on sodium polysulfide melts is being extended. This investigation will determine the conductivity of this molten-salt, high-temperature electrolyte at various temperatures (300 to 350°C) and compositions (Na_2S_3 to Na_2S_5). The data will be analyzed and compared with the differential diffusion coefficients determined in the prior work.

Laplace's equation arises in the description of many systems. Its solution is often expensive and difficult to obtain accurately. Tools are being developed to facilitate its numerical solution. In particular, boundary-integral techniques for axisymmetric and two-dimensional geometries are being developed. Specifically, the current distribution on a band electrode imbedded in an infinitely long cylindrical insulator is being developed. This investigation will be extended by adding a counter-electrode band to the cylinder. This research will play a key role in developing proper techniques in corrosion protection.

Additional work includes an experimental and theoretical impedance study of redox reactions in porous

flow-through electrodes and includes studies of corrosion processes, with an emphasis on developing criteria for adequate corrosion protection.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. A.C. West and J. Newman, "Corrections to Kinetic Measurements Taken on a Disk Electrode," *J. Electrochem. Soc.* **136**, 139 (1989); LBL-24416.
2. W.H. Smyrl and J. Newman, "Current Distribution at Electrode Edges at High Current Densities," *J. Electrochem. Soc.* **136**, 132 (1989); LBL-23905.
3. A.K. Hauser and J. Newman, "Singular Perturbation Analysis of the Faradaic Impedance of Copper Dissolution Accounting for the Effects of Finite Rates of a Homogenous Reaction," *J. Electrochem. Soc.* **136**, 2320 (1989); LBL-25706.
4. A.K. Hauser and J. Newman, "The Effect of Schmidt Number on the Faradaic Impedance of the Dissolution of a Copper Rotating Disk," *J. Electrochem. Soc.* **136**, 2896 (1989); LBL-25721.
5. A.C. West and J. Newman, "Current Distribution Near an Electrode Edge as a Primary Distribution is Approached," *J. Electrochem. Soc.* **136**, 2931 (1989); LBL-26153.
6. A.K. Hauser and J. Newman, "Effect of Finite Rates of a Homogeneous Reaction on the Steady-State Dissolution of Copper in Chloride Solutions," *J. Electrochem. Soc.* **136**, 3249 (1989); LBL-25584.
7. A.K. Hauser and J. Newman, "Potential and Concentration Variations of a Rotating, Supporting Electrolyte," *J. Electrochem. Soc.* **136**, 3319 (1989); LBL-25608.
8. S.D. Thompson and J. Newman, "Differential Diffusion Coefficients of Sodium Polysulfide Melts," *J. Electrochem. Soc.* **136**, 3362 (1989); LBL-23820.
9. A.C. West and J. Newman, "Interpretation of Kinetic Rate Data Taken in a Channel Flow Cell," *J. Electrochem. Soc.* **136**, 3755 (1989); LBL-26621.

LBL Reports

10. A.A. Mason and J. Newman, "Optimization of the LiAl/FeS_x Molten-Salt Batteries," submitted to *J. Electrochem. Soc.*; LBL-26630.
11. A.K. Hauser and J. Newman, "Application of the Macroscopic and Microscopic Impedance Models to the Analysis of the Total Electrochemical Impedance of Copper Dissolution," submitted to *J. Electrochem. Soc.*; LBL-26269.
12. A.K. Hauser and J. Newman, "A Macroscopic-Impedance Model for a Rotating Disk-Electrode," submitted to *J. Electrochem. Soc.*; LBL-26267.
13. A.K. Hauser and J. Newman, "A Microscopic-Impedance Model for a Rotating Disk-Electrode," submitted to *J. Electrochem. Soc.*; LBL-26268.
14. M. Sudoh and J. Newman, "Mathematical Modeling of the Sodium/Iron Chloride Battery," submitted to *J. Electrochem. Soc.*; LBL-26896.
15. A.K. Hauser (Ph.D. Thesis), "Steady-State and Impedance Analysis of Electrochemical Kinetics and Mass Transfer," LBL-27123.
16. A.C. West, J.H. Sukanto, and J. Newman, "A Criterion to Verify Current Distribution Calculations," submitted to *J. Electrochem. Soc.*; LBL-27474.
17. A.C. West and J. Newman, "Current Distribution on Recessed Electrodes," submitted to *J. Electrochem. Soc.*; LBL-28045.
18. A.C. West (Ph.D. Thesis), "Effects of Nonuniform Current and Potential Distributions in Electrochemical Systems," LBL-28076.

Invited Talks

19. A.K. Hauser and J. Newman, "Analysis of Copper Dissolution in Chloride Solutions Using a Microscopic Impedance Model," Electrochemical Society Meeting, Los Angeles, May 9, 1989.
20. T.F. Fuller and J. Newman, "A Concentrated Solution Theory Model of Transport in Solid Polymer Electrolyte Fuel Cells," American Institute of Chemical Engineering, San Francisco, Nov. 6, 1989.
21. J. Newman, "Mass Transfer in Corrosion," American Institute of Chemical Engineers, San Francisco, Nov. 9, 1989.

Health and
Environmental Sciences

Semiconductor Materials and Devices*

Eugene E. Haller, Investigator

INTRODUCTION

The recently achieved ultrahigh purity and crystalline perfection of large germanium single crystals and, to a lesser degree, silicon and gallium arsenide single crystals have led to the discovery of a large number of novel impurity and defect complexes that exhibit energy levels in the band gap of these semiconductors. Understanding the composition and electronic structure of these novel acceptors and donors through the use of sensitive far-infrared spectroscopy techniques and radioactive tracer imaging represents one component of this research effort.

Two factors have helped in identifying the structure and determining the composition of these novel shallow-level centers: (1) unusual electronic ground-state structures with reduced symmetry, and (2) correlation of the concentration of a particular center with the materials involved in the crystal growth and purification processes, such as the crucible material (typically synthetic silica or graphite) and the ambient (typically H_2 , N_2 , or vacuum). One of the major findings is that atomic hydrogen plays an important role in the formation and composition of many of the new impurity complexes. Hydrogen is also found to passivate donors and acceptors in Ge, Si, GaAs, and other compound semiconductors. In Ge, hydrogen forms electrically active centers present at rather low concentrations ($\leq 10^{11} \text{ cm}^{-3}$). The information gained through this research is of immediate use to LBL's semiconductor radiation-detector program, which originated this research.

The use of ultrapure crystals as starting material for specially doped crystals is studied in connection with the development of sensitive far-infrared photoconductors for low-photon-flux applications in outer space and neutron-transmutation-doped germanium for bolometer applications. The high ratio of intentional-dopant concentrations and residual-impurity concentrations has led to photoconductors with very high responsivity working at or close to the photon noise limits.

The close coupling between crystal synthesis and analysis has enabled us to effectively study and use these extremely pure and structurally perfect materials.

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1. Hydrogen-Related Effects in Crystalline Semiconductors (Publication 12)

E.E. Haller

A wealth of experimental and theoretical information regarding the states of hydrogen in crystalline semiconductors has accumulated in recent years. The results illustrate that hydrogen does not preferentially occupy a small number of specific lattice sites but that it binds to native defects and impurities, forming a large variety of neutral and electrically active complexes. The study of hydrogen-passivated shallow acceptors and donors and of partially passivated multivalent acceptors has yielded information on the electronic and real-space structure and on the chemical composition of these complexes. Infrared spectroscopy, ion channeling, hydrogen isotope substitution, and electric-field drift experiments have shown that both static trigonal complexes as well as centers with tunneling hydrogen exist. Total-energy calculations indicate that the charge state of the hydrogen ion that leads to passivation dominates, i.e., H^+ in p-type and H^- in n-type crystals. Recent theoretical calculations indicate that it is unlikely for a large fraction of the atomic hydrogen to exist in its neutral state, a result consistent with the total absence of any electron paramagnetic resonance (EPR) signal. An alternative explanation for this result is the formation of H_2 . Despite the numerous experimental and theoretical results on hydrogen-related effects in Ge and Si, there remains a wealth of interesting physics to be explored, especially in compound and alloy semiconductors.

2. Infrared Absorption Study of Zinc-Doped Silicon (Publication 20)

E. Merk,[†] J. Heyman, and E.E. Haller

We report high-resolution infrared absorption spectra associated with the deep zinc double acceptor in silicon. The optical transitions between ground and bound excited "p-like" states of the neutral helium-like double acceptor Zn^0 center have been observed for the first time (see Figure 2-1). The absorption cross section for the hole transition is found to be very small, of the order of 10^{-17} cm^2 . Energy spacings of the $P_{3/2}$ Rydberg series are very similar to the spacing of the group-III acceptors, suggesting that, in spite of the large ground-state binding energy, effective mass approximation still applies to the bound excited states. This represents one more case where the strong central cell potential does not significantly disturb the neutral helium-like bound excited states. Similar observations have been

Figure 2-1. Excitation spectrum of the neutral helium-like double acceptor Zn in Si at $T = 4.5$ K. The four lines, created by the excitation of one hole from $(1s)^2$ to $(1s, np)$, exhibit energy spacings that are almost identical to the spacings of shallow hydrogenic acceptors in Si. This indicates that the excited holes experience the Coulomb potential of only one charge on the Zn. The second charge is effectively screened by the second deeply bound hole. (XBL 901-140)

made for the less deep neutral double acceptor Be, and for the chalcogen donors S, Se, and Te.

The optical ionization energy of $Zn^{0/-}$ has been determined to be 2575 cm^{-1} (319 meV).

Two additional sets of absorption lines with neutral helium-like spacings related to zinc have been observed at 2130 cm^{-1} and 2758 cm^{-1} . The former set undergoes an isotope shift upon substitution of the hydrogen atmosphere used during the Zn diffusion process with a deuterium atmosphere, indicating the presence of a hydrogen-containing complex.

[†]Swiss National Science Foundation Fellow.

3. Transient Photoconductivity in Ge:Be due to Be^+ Formation (Publication 3)

N.M. Haegel,[†] J.W. Beeman, P.N. Luke, and E.E. Haller

The effect of the formation of the overcharged Be acceptor center Be^+ on transient photoconductive response has been studied in Ge:Be. The response of the photocurrent to step-function changes in photon backgrounds ($\lambda = 40 \mu\text{m}$) is dominated by a slow transient with time constants on the order of 0.1–1.0 sec at temperatures of 2 to 3 K. The activation energy of the hole-trapping phenomenon has been measured to be 4.3 meV (see Figure 3-1). Application of $9.8 \times 10^8 \text{ dyn/cm}^2$ uniaxial stress, sufficient to eliminate Be^+ formation, also eliminates

Figure 3-1. Generation and recombination mechanisms for Be^+ -formation model. Be^+ forms when neutral Be double acceptors capture a third hole. The $1s$ -like ground state can accommodate up to four holes because of the $p_{3/2}$ nature of the top of the valence band. (XBL 901-123)

the slow-transient response (see Figure 3-2). Modeling of the transient response, in a unipolar system where the trapping mechanism is assumed to be hole trapping by Be^0 , results in good agreement with the experimental results.

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Figure 3-2. Photoresponse of Ge:Be to step-function increase in photon flux: (a) unstressed, (b) $2.5 \times 10^8 \text{ dyn/cm}^2$, and (c) $4.9 \times 10^8 \text{ dyn/cm}^2$. Uniaxial stress along [100] splits the valence band top, reducing the maximum number of holes that can be bound to two. Be^+ can no longer be formed under these circumstances. (XBL 901-124)

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. J.L. Hurd, D.L. Perry, B.T. Lee, K.-M. Yu, E.D. Bourret, and E.E. Haller, "Polycrystalline Hexagonal Boron Nitride Films on SiO₂ for III-V Semiconductor Applications," *J. Mat. Res.* **4**, 350 (1989); LBL-25467.
2. T.W. Kenny, P.L. Richards, I.S. Park, E.E. Haller, and J. Beeman, "Bias-Induced Nonlinearities in Neutron-Transmutation-Doped Germanium at ⁴He Temperatures," *Phys. Rev. B* **39**, 8476 (1989); LBL-25633.
3. N.M. Haegel, J.W. Beeman, P.N. Luke, and E.E. Haller, "Transient Photoconductivity in Ge:Be due to Be⁺ Center Formation," *Phys. Rev. B* **39** 3677 (1989).
4. F.M. Rieke, A.E. Lange, J.W. Beeman, and E.E. Haller, "An AC Bridge Readout for Bolometric Detectors," *IEEE Trans. Nucl. Sci.* **NS-36**, 946 (1989); LBL-26498.
5. M. Hamera, W. Walukiewicz, D.D. Nolte, and E.E. Haller, "Dependence of Transition Metal Impurity Levels on Host Composition in III-V Semiconductors," *Phys. Rev. B* **39**, 10114 (1989); LBL-26457.
6. S.K. Cheung, S.P. Kwok, A. Kaleta, K.-M. Yu, J.M. Jaklevic, C.L. Liang, N.W. Cheung, and E.E. Haller, "The Effects of Annealing Encapsulant and Ambient on the Barrier Height of Wn₃GaAs Contact and Self-Aligned Gate Field Effect Transistor Fabrication," *J. Vac. Sci. Technol. B* **6**, 1779 (1988).
7. K. Unterrainer, M. Nishsoontron, M. Helm, E. Gornik, and E.E. Haller, "Single Mode Operation of the p-Ge FIR Laser," *Infrared Phys.* **29**, 357 (1989).
8. E. Merk, J. Heyman, and E.E. Haller, "Infrared Spectroscopy of the Neutral Zinc Double-Acceptor in Silicon," *Solid State Commun.* **72**, 851 (1989).

Other Publications

9. W. Walukiewicz and E.E. Haller, "Fermi Energy Dependent Formation of Native Defects in Semiconductors," in *Proc. 19th Int. Conf. on the Physics of Semiconductors*, W. Zawadzki, Ed., Inst. of Physics, Polish Acad. of Sciences, 1988, p. 975; LBL-25013.
10. T. Yamamoto, H. Sukebe, S. Komiyama, T. Kurosawa, and E.E. Haller, "Evidence for Bunching of Streaming Carriers in Momentum Space," in *Proc. 19th Int. Conf. on the Physics of Semiconductors*, W. Zawadzki, Ed., Inst. of Physics, Polish Acad. of Sciences, 1988, p. 1451.
11. B.L. Gel'mont, V.G. Golubev, V.I. Ivanov-Omskii, G.I. Kropotov, and E.E. Haller, "Magnetospectroscopic Studies of the D(H₂O) Complex in Germanium," in *Proc. 19th Int. Conf. on the Physics of Semiconductors*, W. Zawadzki, Ed., Inst. of Physics, Polish Acad. of Sciences, 1988, p. 1281.
12. E.E. Haller, "Hydrogen-Related Effects in Crystalline Semiconductors," in *Proc. 3rd Int. Conf. on Shallow Impurities in Semiconductors*, B. Monemar, Ed., Inst. Phys. Conf. Ser. **95**, 425 (1989); LBL-25708.
13. D.D. Nolte, W. Walukiewicz, M. Hamera, and E.E. Haller, "Direct Measurement of Band-Edge Hydrostatic

Deformation Potentials in Semiconductors," in *Proc. 19th Int. Conf. on the Physics of Semiconductors*, W. Zawadzki, Ed., Inst. of Physics, Polish Acad. of Sciences, 1988, p. 893; LBL-25598.

14. E.E. Haller, H. Baumann, J. Beeman, W.L. Hansen, P.N. Luke, M. Lutz, C.S. Rossington, and I.C. Wu, "Germanium Blocked Impurity Band (BIB) Detectors," in *Proc. 3rd IR Detector Technology Workshop*, Feb. 7-9, 1989, NASA Techn. Memor. 102209, C. McCreight, Ed., 1989, p. 85; LBL-26814.
15. J. Beeman, E.E. Haller, W.L. Hansen, P.N. Luke, and P.L. Richards, "Stressed Ge:Ga Photoconductors for Space-Based Astronomy," in *Proc. 3rd IR Detector Technology Workshop*, Feb. 7-9, 1989, NASA Techn. Memor. 102209, C. McCreight, Ed., 1989, p. 5; LBL-26784.
16. N. Wang, F.C. Wellstood, B. Sadoulet, E.E. Haller, and J. Beeman, "Electrical and Thermal Properties of Neutron-Transmutation-Doped Ge at 20 mK," *Phys. Rev. B* (in press).
17. G.J. Stacy, J.W. Beeman, E.E. Haller, N. Geis, A. Poglitsch, and M. Rumitz, "Stressed Detector Arrays for Airborne Astronomy," in *Proc. 3rd IR Detector Workshop*, Feb. 7-9, 1989, NASA Techn. Memor. 102209, C. McCreight, Ed., 1989, p. 247.

LBL Reports

18. E.E. Haller, "Hydrogen-Related Phenomena in Crystalline Germanium," in *Hydrogen in Semiconductors*, J. Pankove and N. Johnson, Eds., Academic Press, Orlando, FL (in press); LBL-27043.
19. D.E. Bliss, W. Walukiewicz, D.D. Nolte, and E.E. Haller, "Absolute Pressure Dependence of the Second Ionization Level of EL2 in GaAs," *MRS*, Boston, Nov. 27-Dec. 2, 1989; accepted by *Mat. Res. Soc. Proc.*; LBL-27522.
20. E. Merk, J. Heyman, and E.E. Haller, "Infrared Absorption of Zn-Doped Silicon," accepted by *Mat. Res. Soc. Proc.*; LBL-28206.

Invited Talks

21. E.E. Haller, "Germanium Blocked Impurity Band (BIB) Detectors," NASA Ames Research Center, Moffett Field, CA, Feb. 9, 1989.
22. E.E. Haller, "Hydrogen in Semiconductors," 7th Lund Deep Level Conference, Saltsjöbad, Sweden, June 7, 1989.
23. E.E. Haller, "Germanium Far-Infrared Photoconductors," NASA Langley Research Center, Norfolk, VA, June 19, 1989.
24. E.E. Haller, "Far-IR BIB Detectors," NASA Langley Research Center, Norfolk, VA, June 20, 1989.
25. E.E. Haller, "Hydrogen in Semiconductors," 1989 Electronic Materials Conference, MIT, Cambridge, MA, June 23, 1989.
26. E.E. Haller, "Detecting Photons from MeV to meV's," Physics Department, University of California at Berkeley, Sept. 20, 1989.
27. E.E. Haller, "What Is a Materialist," MSEA-SEMPE, University of California at Berkeley, Sept. 28, 1989.

Exploratory Research
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Raman Studies of Surfaces and Materials*

Gerd M. Rosenblatt, Investigator

INTRODUCTION

The purpose of this project is to utilize and develop Raman and related optical techniques for the study of surfaces and materials. The project uses unenhanced Raman spectroscopy to study surface and near-surface composition; to provide new information concerning rotational and vibrational energy levels, dynamics, and reactivity of molecules adsorbed on a variety of surfaces; to study fundamental processes under both ultrahigh vacuum (UHV) conditions and at chemically important pressures and temperatures; and to characterize technologically important materials. Raman instrumentation developed for this project makes use of an imaging photomultiplier detector to achieve the sensitivity required to obtain unenhanced Raman spectra from adsorbed monolayers on well-characterized surfaces. By explicitly utilizing the two-dimensional detection capability of the imaging photomultiplier, spatially resolved Raman spectra are obtained; these provide unique, spatially resolved vibrational data for chemical mapping of surface and near-surface composition with unprecedented speed at high resolution. The sensitivity of the apparatus allows the study by Raman spectroscopy of materials that were heretofore impossible.

1. Raman Characterization of High-Temperature Materials using an Imaging Detector (Publication 6)

G.M. Rosenblatt and D.K. Veirs

The characterization of materials by Raman spectroscopy has been impacted by recent technological advances in light detectors. Modern imaging detectors provide substantial new capabilities in two areas: (1) enhanced signal-to-noise (S/N) ratio and (2) spectral "imaging" of an illuminated sample. Imaging photomultipliers have inherent low background and true photon-counting capability. They thus provide both increased sensitivity and dramatic decreases in detector dark noise. The combination of increased sensitivity and

reduced noise (i.e., enhanced S/N) allows smaller amounts of material to be analyzed. These detectors also enable production of two-dimensional maps of chemical composition by rapid acquisition and analysis of Raman spectra. A one-dimensional profile of the chemical composition along a thin laser-illuminated line can be obtained during one data acquisition and analysis cycle by imaging the illuminated line on the spectrometer entrance slit so that spatial resolution is attained along the y axis of the detector while the spectra are dispersed along the x axis. Two-dimensional maps of the chemical composition can be built up from successive one-dimensional profiles by translating the sample across the illumination line.

The combination of enhanced S/N and spatial information allows Raman spectroscopy to be used for materials characterization hitherto difficult or impossible. We discuss three applications: characterization of amorphous carbon films (~30 nm thick) and single carbon fibers (8 μm diameter), and mapping of phase-transformation zones in partially stabilized zirconia.

The Raman spectra of amorphous carbon films and single graphitic fibers are dominated by a peak (G) near 1580 cm^{-1} associated with crystalline graphite and a peak (D) near 1380 cm^{-1} associated with disordered graphite; line positions and widths are related to the bonding. The ratio of the intensities of the D and G lines, I_D/I_G , correlates with microcrystallite size; intensity ratios less than one yield a linear relation with the inverse of the domain size. Carbon films used as protective overcoats on computer "hard disks" are found to be composed of microcrystallites of less than 2 nm with 5% sp^3 bonds. Upon annealing, the sp^3 bond percentage drops essentially to 0% as the grains grow.

Carbon fibers are widely used as structural reinforcement because of their strength-to-weight ratio. Fiber properties are anisotropic and dependent upon their high-temperature processing. The I_D/I_G ratios of single carbon fibers annealed at successively higher temperatures steadily decrease (see Figure 1-1). The microcrystallite domain size of the carbon fibers nearly doubles upon increasing the annealing temperature from 2400°C to 2800°C .

Partially stabilized zirconia is an important high-strength, low-density toughened ceramic. When a crack propagates in this material, the metastable tetragonal zirconia particles martensitically transform to the monoclinic phase in the high stress fields associated with the crack tip, forming a transformed zone surrounding the crack and crack tip. Using the imaging Raman spectrometer, the relative fraction of monoclinic phase along a laser-illuminated, slit-like region perpendicular to the crack is determined. The relative phase percentage is computed at each of 1024 points along the illumination line

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Figure 1-1. Increasing annealing temperatures change the Raman spectra of single carbon fibers. Changes in the relative intensity of the observed bands reflect growth of the graphite microcrystallites at higher annealing temperatures. (XBL 891-223)

by comparing the observed spectrum for that point with the spectra of the pure phases (see Figure 1-2), yielding a one-dimensional profile of the relative fraction of monoclinic phase as a function of position. Automatically translating the sample and obtaining successive profiles, a two-dimensional map of the relative fraction of monoclinic phase can be produced in a few hours.

Figure 1-3 shows a map of a transformed zone surrounding a crack, the product of analysis of 65,000 Raman spectra. The stress history of the specimen is revealed in the extent and degree of transformation of the transformed zone; regions where the crack propagated by application of unusually large-amplitude cyclic loads show a particularly large degree and extent of phase transformation, which remains after the crack tip moves on. Raman spectroscopy provides unique information for these

Figure 1-2. Relative phase percentage of the observed spectrum computed from the spectra of the "pure" components. (XBL 901-151)

Figure 1-3. Results from the analysis of 65,000 Raman spectra are used to construct a map of the phase distribution surrounding a crack in partially stabilized zirconia. (XBL 891-220)

fracture studies because it yields both the degree and spatial extent of the martensitic transformation. The technique can reveal transformations of less than 1% and achieve a spatial resolution below 5 μm .

The software, ChemMap, that has been written to acquire, analyze, and display two-dimensional chemical maps has been extensively tested, as well as documented and copyrighted, and its commercialization is being explored as part of LBL's technology transfer efforts.

2. Work in Progress

Preliminary investigations of the effects of laser-power flux on a single graphite fiber indicate that interactions between the laser beam and the sample result in substantial physical and chemical changes in the sample. Areas identified for further work include laser heating of the sample, the effect of temperature on the Raman spectra, oxidative erosion, irreversible and reversible changes, and mapping the extent of the changes away from the impinging laser beam. The temperature dependence of the Raman spectra of highly ordered pyrolytic graphite (HOPG) is being studied in order to understand the observed changes in the less-well-ordered graphite fibers. Other collaborative projects that are being pursued actively include Raman studies of hard carbon films, "diamond-like" films, and diamond films. Further development of Raman mapping, including collaborative studies of transformed zones in zirconia, also is being pursued.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. V.K.F. Chia, D.K. Veirs, and G.M. Rosenblatt, "Cryogenic Sample Manipulator for Multipurpose Sample Analysis," *J. Vac. Sci. Technol. A*, **7**, 108 (1989); LBL-24865.
2. J.R. Stephens and G.M. Rosenblatt, "A Re-examination of Energy Accommodation Experiments using the Vibrating Surface Technique," *J. Chem. Phys.* **90**, 2513 (1989).
3. V.K.F. Chia, D.K. Veirs, and G.M. Rosenblatt, "Ultrahigh Vacuum Apparatus for Unenhanced Surface Spectroscopy and Characterization at Cryogenic Temperatures," *Rev. Sci. Instrum.* **60**, 1161 (1989); LBL-24567.
4. D.K. Veirs, V.K.F. Chia, and G.M. Rosenblatt, "Unenhanced Surface Raman Spectroscopy of Nitrogen Physisorbed on Ag(111)," *Langmuir* **5**, 633 (1989); LBL-24566.
5. R.H. Dauskardt, R.O. Ritchie, and D.K. Veirs, "Spatially Resolved Raman Spectroscopy in the Study of Transformed Zones in PSZ," *J. Am. Ceram. Soc.* **72**, 1124 (1989); LBL-25251.

LBL Reports

6. G.M. Rosenblatt and D.K. Veirs, "Raman Characterization of High Temperature Materials using an Imaging Detector," *High Temp. Sci.* (in press); LBL-26130.

Invited Talks

7. D.K. Veirs[†] and G.M. Rosenblatt, "Recent Developments in Compositional Mapping using Raman Spectroscopy," ACS Pacific Conference, San Francisco, CA, Oct. 1988.
8. G.M. Rosenblatt[†] and D.K. Veirs, "Recent Developments in Raman Spectroscopy of High Temperature Materials," 25th Bay Area Conference on High Temperature Science and Technology, Berkeley, CA, Nov. 1988.
9. D.K. Veirs[†] and G.M. Rosenblatt, "Recent Developments using Imaging Detectors for Raman Characterization of High Temperature Materials," Chemical and Laser Sciences Division Seminar, Los Alamos, NM, Feb. 1989.
10. G.M. Rosenblatt[†] and D.K. Veirs, "Recent Developments using Imaging Detectors for Raman Characterization of High Temperature Materials," 6th International Conference on High Temperatures—Chemistry of Inorganic Materials, Gaithersburg, MD, April 1989.
11. G.M. Rosenblatt, "Recent Reports of 'Cold' Fusion," Sixth International Conference on High Temperatures, Gaithersburg, MD, April 1989.
12. G.M. Rosenblatt, "From Cyclotrons to Synchrotrons, from Protons to Photons," Physics Department, Vrije Universiteit Brussel, Brussels, Belgium, May 1989.
13. D. Czechowicz[†] and G.M. Rosenblatt, "Vaporization Thermodynamics in the Uranium-Tellurium System," 13th Midwest High Temperature and Solid State Chemistry Conference, Binghamton, NY, June 1989.
14. D.K. Veirs,[†] G.M. Rosenblatt, and J.W. Ager III, "Raman Spectroscopy of Adsorbed Films and Advanced Materials," Chemistry Seminar, University of California, Davis, Sept. 1989.

[†]Presenting author.

Characterization of Materials from Nanocrystalline Particles and Composites by Transmission Electron Microscopy (TEM)*

U. Dahmen and K.H. Westmacott, Investigators

INTRODUCTION

Materials with extremely small grain size, in the range of a few Angstroms to a few hundred Angstroms, are termed nanocrystals or nanocomposites. By virtue of their very high grain-boundary area, such materials show unusual properties, such as greatly enhanced diffusivity, low sintering temperatures, limited grain growth, and shifts in magnetic properties.

Nanocomposites with a narrow range of size distributions and with varying degrees of texture are of particular interest because of their potential for controllable packing density and anisotropy. Ceramic materials of this nature can be produced by thermal-decomposition reactions. The resulting porous microstructure may be considered a composite of small oriented crystallites (nanocrystals) and pores.

The highest degree of texture is obtained by ionized-cluster-beam deposition of metals on a single-crystal substrate, a technique that allows the formation of thin films with unique continuous bicrystal structure.

In this program we explore new materials synthesized from ultrafine grains (nanocrystals) or clusters, to study the potential for producing novel microstructures with unique properties, and to conduct a detailed microstructural investigation to understand effects of processing variables.

1. Atomic Structure of a $\Sigma 99$ Grain Boundary in Aluminum: A Comparison Between Atomic-Resolution Observation, Pair Potential, and Embedded-Atom Simulations (Publication 6)

U. Dahmen, C.J.D. Hetherington, M.A. O'Keefe, K.H. Westmacott, M.J. Mills,[†] M.S. Daw,[‡] and V. Vitek[§]

Recent improvements in the resolution limit of transmission electron microscopes to below 0.2 nm allow direct imaging of the atomic structure of grain boundaries in close-

packed metals and detailed comparison with theoretical predictions. This work describes such a study for a symmetrical $\Sigma 99$ {557} $\langle 110 \rangle$ tilt boundary in aluminum. Although comprehensive comparisons between high-resolution images and calculated structures have been made in the past, this is the first time such a comparison has been made for a high- Σ boundary and at this level of detail. It is also the first time that calculations of the same boundary by pair potentials and the embedded-atom method have been compared quantitatively, both to each other and to experimental observation.

Figure 1-1 shows that the match between the experimental and calculated images is excellent for both calculated structures. Because it was possible to discard unambiguously a number of other structures found in the process of computer modeling as clearly mismatched with the observation, a comparison of this kind is an accurate measure of the quality of the match between theory and experiment. This point is important, since it demonstrates that high-resolution microscopy now allows the experimental distinction between different atomic-boundary structures in close-packed metals. However, the structures calculated by the two theoretical approaches were so similar that it was not possible within the experimental limitations at this time to decide which of the two models describes the observed structure more closely. The fact that, in a short

Figure 1-1. Comparison of images simulated from (a) the embedded-atom method (EAM) and (c) the pair potential (PP) structure with the averaged experimental image (b). Superposition of the images shown in (a)-(c) in reversed and enhanced contrast over the experimental image illustrates the match for the EAM (d) and PP (e). This type of comparison is validated by (e), where the image in reversed and enhanced contrast is overlaid on itself (although note that, due to the response of the photographic emulsion, the black spots are larger than in the neighboring images). (XB'3 890-10224)

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facet of such a high- Σ bicrystal, the two models appear to converge on the same structure as that observed is an encouraging result, validating both the theoretical and experimental approaches that have been adopted.

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2. Fundamental Studies of Grain-Boundary Structure and Properties in ICB Aluminum (Publication 2)

K.H. Westmacott and U. Dahmen

Thin films prepared by the ionized-cluster-beam (ICB) technique, pioneered at Kyoto University, are of great interest for both their fundamental structure and properties and their potential for practical applications. ICB research has burgeoned in the last few years, with emphasis concentrated on understanding the physics of the deposition process, determining the size and structure of clusters, correlating structure and properties, exploring the range of materials that can be prepared by the technique, and attempting to use the films in electronic device applications. At Berkeley a research program has been initiated, in collaboration with Professor Yamada and his colleagues at Kyoto University, to investigate a different aspect of ICB films. We are exploiting the unique bicrystal microstructure that forms with some thin-film/substrate combinations to conduct fundamental investigations of grain-boundary structure and properties.

High-resolution TEM also provides a valuable tool for examining the morphology and structure of individual metal clusters. For this purpose, an amorphous carbon-coated specimen grid was used as the substrate. Because of the small cluster size, the particles in the as-recorded film image are barely discernable (see Figure 2-1a). However, by digitizing and processing, the image of the metal cluster can be significantly enhanced relative to that of the

substrate, as seen in Figure 2-1b, c, and d. A variation in cluster size and shape is found, and the substructure varies from single crystalline (b) to more complex particles with a preferred orientation (c, d). It is probable that the complex particles are in fact multiple clusters and that these are present on the substrate in much greater concentration than the single clusters.

3. Work in Progress

An apparatus for the production of nanocrystalline materials by the spark-erosion technique has been constructed and is being employed to prepare precursor materials for decomposition reactions. X-ray and TEM analyses show that, depending on electrode composition and erosion conditions, pure metal and alloy hydroxide powders such as $\text{Al}(\text{OH})_3$ and $\text{Mg}_4\text{Al}_2(\text{OH})_{14} \cdot 3\text{H}_2\text{O}$ can be produced.

1989 PUBLICATIONS AND REPORTS

Other Publications

1. K.H. Westmacott and U. Dahmen, "A Comparative HVEM Study of ICB-Deposited Aluminum Films," in *Proc. 47th Annual EMSA Meeting*, San Antonio, TX, G.W. Bailey, Ed., San Francisco Press, Inc., 1989, p. 642; LBL-26919.
2. K.H. Westmacott and U. Dahmen, "Fundamental Studies of Grain Boundary Structure and Properties," in *Proc. ISIAT Conf.*, Tokyo, Japan, June 5-7, 1989; LBL-27187.
3. K.H. Westmacott and U. Dahmen, "High Voltage/High Resolution Studies of Metal and Semiconductor Interfaces," in *Proc. Int. Symp. on Electron Microscopy in Plasticity*, Holzhau, German Democratic Republic, 1989, p. 109; LBL-26274.
4. S. Tanaka, H. Usui, U. Dahmen, K.H. Westmacott, and I. Yamada, "Microstructure of Epitaxial Al Films Deposited on Si by ICB Method," in *Proc. ISIAT Conf.*, Tokyo, Japan, June 5-7, 1989, p. 281.

Figure 2-1. High-resolution micrographs of individual Ag clusters deposited on a carbon substrate. An as-recorded image is shown in (a), and computer-enhanced images are shown in (b), (c), and (d). The same cluster is seen as recorded in (a) and Fourier filtered in (b). (XBB 895-4012)

5. I. Yamada, H. Usui, S. Tanaka, U. Dahmen, and K.H. Westmacott, "Atomic Resolution Study of the Structure and Interface of Aluminum Films Deposited Epitaxially on Silicon by ICB Method," in *Proc. 36th Nat. Am. Vac. Soc. Symp.*, Boston, MA, Nov. 21-27, 1989, p. 47.

LBL Reports

6. U. Dahmen, C.J.D. Hetherington, M.A. O'Keefe, K.H. Westmacott, M.J. Mills, M.S. Daw, and V. Vitek, "Atomic Structure of a $\Sigma 99$ Grain Boundary in Aluminum: A Comparison Between Atomic-Resolution Observation, Pair Potential and Embedded Atom Simulations," submitted to *Phys. Rev. Lett.*; LBL-28123.
7. A.M. O'Keefe and U. Dahmen, "Simulated Image Maps for Use in Experimental High Resolution Microscopy," *MRS Symp. Proc.* (in press); LBL-27503.
8. K.H. Westmacott and U. Dahmen, "Studies of Faceting by High Voltage/High Resolution Microscopy," in *Proc. Indo-U.S. Workshop on Interfaces: Structure and Properties*, Bangalore, India, Dec. 1989 (in press); LBL-28389.

Invited Talks

9. U. Dahmen and K.H. Westmacott, "Structure of Near- $\Sigma 17$ $\langle 110 \rangle$ Tilt Boundaries in Aluminum," *Scanning '89 EM West*, Long Beach, CA, Apr. 5-7, 1989.

10. K.H. Westmacott and U. Dahmen, "Fundamental Studies of Grain Boundary Structure and Properties in ICB Aluminum," *ISIAT '89 Conf.*, Tokyo, Japan, June 5-6, 1989.
11. K.H. Westmacott and U. Dahmen, "A Comparative HVEM Study of ICB-Deposited Aluminum Films," *EMSA annual meeting*, San Antonio, TX, Aug. 7-11, 1989.
12. U. Dahmen, V. Vitek, M.A. O'Keefe, and K.H. Westmacott, "The Structure of an Asymmetrical $\Sigma 17 \langle 110 \rangle$ Tilt Boundary in Aluminum: A Comparison of Experimental Observation and Atomistic Calculation," *International Congress on Intergranular and Interphase Boundaries in Materials*, Paris, Sept. 4-8, 1989; LBL-27185abs.
13. K.H. Westmacott, "Structure and Properties of 90° Tilt Boundaries in Al Bicrystals," *MPI*, Stuttgart, Federal Republic of Germany, Oct. 4, 1989.
14. U. Dahmen, "TEM Studies of Interfaces and Phase Transformations," *Exxon Research Laboratories*, Annandale, NJ, Oct. 6, 1989.
15. K.H. Westmacott and U. Dahmen, "High Voltage/High Resolution Studies of Metal and Semiconductor Interfaces," *International Symposium on Electron Microscopy in Plasticity*, Holzhau, German Democratic Republic, Oct. 8-10, 1989.
16. M.A. O'Keefe and U. Dahmen, "Simulated Image Maps for Use in Experimental High Resolution Microscopy," *MRS Fall Meeting*, Boston, MA, Nov. 27-Dec. 1, 1989; LBL-27503.

Structure-Property Relationships for Aqueous Gels*

J.M. Prausnitz, Investigator

INTRODUCTION

The goal of this work is to develop a molecular-thermodynamic framework for describing the phase behavior of aqueous polymer gels as a function of network and solution conditions, i.e., to elucidate structure-property relationships for hydrogels. Gels exhibiting large, reversible-volume transitions in response to changes in solution conditions are being investigated in several novel applications; however, progress is often limited by the need to determine (experimentally) the synthesis conditions that result in a gel with the desired swelling properties. By developing a quantitative framework for guiding gel design, this work will contribute to the efficient implementation of gels in new technologies.

Our approach is, first, to obtain a fundamental understanding of the factors that induce and influence volume transitions in hydrogels, and second, to use that knowledge to develop a molecular-thermodynamic model to describe (and predict) those transitions.

1. Thermodynamics of Aqueous Systems Containing Hydrophilic Polymers or Gels (Publication 1)

M.M. Prange, H.H. Hooper, and J.M. Prausnitz

We develop an oriented-lattice model for describing mixing effects in aqueous polymer solutions. This model was applied successfully for describing vapor-liquid and liquid-liquid equilibria in uncrosslinked aqueous polymer solutions, and for describing temperature-induced volume collapse of uncharged N-isopropylacrylamide (NIPA) gel.

2. Swelling Equilibria for Ionized Polyacrylamide Hydrogels and Ionized Temperature-Sensitive Gels in Water and in Aqueous Salt Solutions (Publications 2 and 3)

H.H. Hooper, J.P. Baker, H.W. Blanch, S. Beltran, and J.M. Prausnitz

Elasticity theories are usually applied for describing the properties of networks prepared in bulk. In Publication 2 we evaluate the ability of existing elastic equations of state to describe the gel-composition dependence of swelling equilibria for networks prepared in solution. The effect of crosslink density on swelling equilibria is described semiquantitatively; however, existing theories are unable to describe the dependence of swelling equilibria on monomer concentration at preparation.

To study systematically the effects of gel charge density and solution conditions on polyelectrolyte swelling equilibria, we planned sequential studies for four series of (increasingly complex) hydrogel systems. First, we considered isothermal swelling equilibria for a gel containing a strong electrolyte (Publication 2); for this system, we isolated attention on the effects of gel charge and solution ionic strength on swelling equilibria. Second, we considered a temperature-sensitive gel containing a strong electrolyte (Publication 3); in this study, the combined effects of temperature, gel charge, and solution ionic strength were examined. The third and fourth systems will consider gels containing weak electrolytes (i.e., pH-sensitive gels); we will examine the swelling behavior of isothermal, and then temperature-sensitive, gels containing weak electrolytes.

All existing theories of gel swelling are based on the Flory-Rehner assumption¹ that when a gel swells (or deswells) the change in Gibbs energy is a sum of three contributions:

$$\Delta G = \Delta G_{\text{mix}} + \Delta G_{\text{elas}} + \Delta G_{\text{ion}}, \quad (1)$$

where subscript *mix* denotes the contribution from polymer/solvent mixing, subscript *elas* denotes elastic effects from deforming the network from its relaxed state, and subscript *ion* denotes all contributions resulting from bound ions on the gel network and from added electrolyte. When all the terms in Eq. (1) are known (as a function of gel composition and solution conditions), the equilibrium degree of swelling may be determined.

*This work was supported by the Director's Exploratory Research and Development Funds of the Lawrence Berkeley Laboratory under Contract No. DE-AC03-76SF00098.

To provide an initial extension of our swelling model to ionized gels, we have used ideal Donnan equilibria² for ΔG_{ion} in Eq. (1). Publication 2 indicates that this extension of the swelling model provides semiquantitative predictions for the effects of gel charge and solution ionic strength on isothermal swelling equilibria of ionized acrylamide gels. In Publication 3, the model is also shown to describe well the effects of gel charge and solution ionic strength on the temperature-induced collapse of ionized NIPA gels.

1. P.J. Flory and J. Rehner, *J. Chem. Phys.* **11**, 541 (1943).
2. P.J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.

3. Monte Carlo Simulations of Hydrophobic and Partially Ionized Polyelectrolytes (Publications 4 and 5)

H.H. Hooper, H.W. Blanch, S. Beltran, A.P. Sassi, and J.M. Prausnitz

As a complement to our theoretical and experimental studies, we have used Monte Carlo simulation to examine, on a fundamental level, the factors that influence gel volume transitions. Isolated polymers undergo coil-globule transitions that are analogous to gel-volume transitions; thus, the factors that induce and influence these transitions can be examined at the molecular level by considering the behavior of the isolated polymer chain. We have used Monte Carlo computer simulation to investigate the configurational properties of isolated polyelectrolytes in a dielectric continuum.

In Publication 4, we consider the behavior of "hydrophilic" polyelectrolytes, i.e., chains that do not interact through dispersion forces. We compared simulation results with two analytical theories used frequently for describing the electrostatic contribution to gel swelling. The two theories showed large discrepancies when compared with "exact" (simulated) results for the model on which they are based. This result provides a negative, but useful, conclusion: that previous attempts to describe the effects of intrachain fixed-ion repulsions on gel swelling are inaccurate. In Publication 5, we investigate the behavior of polyelectrolytes having attractive segment-segment interactions that compete with repulsive coulombic interactions. We observed large structural transitions in these "hydrophobic" polyelectrolytes in response to an increase in chain ionization. The transitions appear analogous to pH-induced volume transitions in hydrophobic

polyelectrolyte gels, and may provide a simple theoretical explanation for such volume transitions.

4. Work in Progress

The failure of existing theories to consider the contribution of entanglements to network elasticity probably causes the poor agreement of these theories with swelling equilibria for gels prepared at different monomer concentrations. We are currently performing stress-strain measurements to determine the elastic properties for a series of ionized acrylamide gels prepared with different monomer concentrations. These stress-strain data will be used to quantify the effect of monomer concentration (and entanglements) on elasticity, and to account for these effects in the elastic contribution to gel swelling.

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. M.M. Prange, H.H. Hooper, and J.M. Prausnitz, "Thermodynamics of Aqueous Systems Containing Hydrophilic Polymers or Gels," *AIChE J.* **35**, 803 (1989); LBL-26723.
2. H.H. Hooper, J.P. Baker, H.W. Blanch, and J.M. Prausnitz, "Swelling Equilibria for Ionized Polyacrylamide Hydrogels," *Macromolecules* **23**, 1096 (1990); LBL-27284.
3. S. Beltran, H.H. Hooper, H.W. Blanch, and J.M. Prausnitz, "Swelling Equilibria for Ionized Temperature-Sensitive Gels in Water and in Aqueous Salt Solutions," *J. Chem. Phys.* **92**, 2061 (1990); LBL-27572.

LBL Reports

4. H.H. Hooper, H.W. Blanch, and J.M. Prausnitz, "Configurational Properties of Partially-Ionized Polyelectrolytes from Monte Carlo Simulation," submitted to *Macromolecules*; LBL-28665.
5. H.H. Hooper, S. Beltran, A.P. Sassi, H.W. Blanch, and J.M. Prausnitz, "Monte Carlo Simulations of Hydrophobic Polyelectrolytes. Evidence for a Structural Transition in Response to Increasing Chain Ionization," submitted to *J. Chem. Phys.*; LBL-28677.
6. H.H. Hooper, H.W. Blanch, and J.M. Prausnitz, "Molecular Thermodynamics of Aqueous Polymers and Gels," in *Absorbent Polymer Technology*, L. Brannon-Peppas and R. Harland, Eds., Elsevier Publishers, Amsterdam (in press); LBL-28666.

Work for
Others

UNITED STATES OFFICE OF NAVAL RESEARCH

High- T_c Superconductivity*

Vladimir Z. Kresin, Investigator

INTRODUCTION

This research is concerned with different aspects of high- T_c superconductivity, such as the origin of high T_c , properties of the new high- T_c oxides, and applications.

A unified approach to the description of high- T_c oxides has been developed. This approach enables one to correlate normal and superconducting properties of oxides and to evaluate the strength of the interactions. It is directly related to the origin of high T_c . Several predictions, such as existence of the Fermi surface and the presence of the peculiar low-lying plasmon branch, were verified experimentally.

The proximity effect in the presence of high- T_c film has been analyzed. From these results, it has been predicted that proximity systems can be used to obtain a high critical current and to make a three-terminal device (see Publication 4).

1. Major Normal and Superconducting Parameters of the High- T_c Oxides. Strength of the Coupling (Publications 1, 5, 6, 10, and 13)

V.Z. Kresin and S.A. Wolf

The major normal and superconducting parameters of high- T_c oxides have been evaluated. The analysis, based on Fermiology, is carried out in reciprocal space: the anisotropy of the system is reflected in the shape of the Fermi surface. The analysis is valid for any form of the Fermi curve. The small value of the Fermi energy and the Fermi velocity obtained, along with the presence of a layered structure, are the key features of the cuprates. The coherence length ξ_0 is evaluated and appears to be short. The value of H_{c2} is calculated in a self-consistent way. The method of evaluation of the strength of the electron-phonon

coupling is developed and leads to a strong coupling that, however, is not sufficient to give the observed value of T_c . The effects of anisotropy and multigap structure are discussed.

2. Spectroscopy of Layered Conductors and Phonon-Plasmon Mechanisms of Superconductivity (Publications 2, 3, 7, 10, and 12)

V.Z. Kresin and H. Morawitz

The recently discovered layered copper oxide high- T_c superconductors are discussed as models of a layered electron gas with highly anisotropic collective modes (layer plasmons). Our view that a combined phonon-plasmon pairing interaction is the mechanism for the high transition temperatures is presented, together with the appropriate dielectric function describing the electron collective response. The implications of this model for the interpretation of optical (infrared and optical absorption, reflectivity, and Raman scattering) and related spectroscopies, such as electron and positron loss, are given. In particular, temperature-dependent loss features are shown to arise from the lowest branch of the layer plasmons.

In contrast to isotropic three-dimensional metals, charged-particle (electron or positron) losses in layered conducting materials depend strongly on temperature. It is demonstrated that this effect arises from specific features of the plasmon band in such systems. This prediction can be checked experimentally.

3. High- T_c Superconductor in an ac Field (Publication 8)

V.Z. Kresin

The behavior of high- T_c oxides in an alternating field is studied. The short coherence length and the layered structure require an unconventional microscopic analysis. The complex conductivity $\sigma(\omega, k)$ is evaluated. The frequency and temperature dependences of the impedance are obtained (in the region of small frequencies). The effect of impurities is discussed. The microwave properties of the proximity system S_h -N (where S_h and N are high- T_c and normal films, respectively) are discussed.

*This work was supported by the U.S. Office of Naval Research under Contract No. N00014-86-F0015 through an agreement with the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

4. Proximity Effect and High- T_c Superconductivity (Publications 4, 13, and 14)

V.Z. Kresin

A proximity system containing HT films (where HT is a high- T_c superconductor), which allows one to take advantage of the properties of both HT and conventional materials, has been developed.

The properties of Josephson junctions containing the proximity system S_h -N (where S_h is a high- T_c film and N is a normal film) are analyzed. The amplitude of the Josephson current appears to be largest for the S_h -N-I- S_c junction (where S_c is a conventional superconductor and I is an insulator). Junctions containing semiconductor films are promising for field-effect applications.

the Phonon-Plasmon Mechanism of Superconductivity," in *Studies of High Temperature Superconductors*, A.V. Narlikar, Ed., Nova, NY, 1989, p. 305.

10. V.Z. Kresin and S.A. Wolf, "Electron-Phonon Coupling, Gap Anisotropy and Multigap Structure in the New High T_c Cuprates," in *High Temperature Superconductors*, T. Akachi, J. Cogordan, and A. Valladares, Eds., World, Singapore, 1989, p. 23.
11. H. Morawitz and V.Z. Kresin, "Oxygen Double Well Potential and Strong Carrier-Phonon Coupling in the High T_c Oxides," *Bull. Am. Phys. Soc.* **34**, 510 (1989).
12. V.Z. Kresin and H. Morawitz, "On the Phonon-Plasmon Mechanism of High T_c ," *Bull. Am. Phys. Soc.* **34**, 511 (1989).
13. V.Z. Kresin and S.A. Wolf, "Fermiology of High T_c Films and the Proximity Effect," in *Science and Technology of Thin Film Superconductors*, R. McConnell and S.A. Wolf, Eds., Plenum, New York, 1989, p. 527.
14. V.Z. Kresin, "Proximity Effect and High T_c Superconductivity," ISS '89 Procs., Japan (in press).

1989 PUBLICATIONS AND REPORTS

Refereed Journals

1. V.Z. Kresin and S.A. Wolf, "A Method for Evaluating the Electron-Phonon Coupling in Cuprates from Heat Capacity Measurements," *Physica C* **158**, 76 (1989).
2. V.Z. Kresin and H. Morawitz, "Charged Particle Energy Loss in Layered Media," *Mod. Phys. Lett. B* **3**, 183 (1989).
3. V.Z. Kresin and H. Morawitz, "Spectroscopy of the Layered High-Temperature Superconductors and Their Collective Plasmon Modes—A Model for Phonon- and Plasmon-Induced Pairing," *J. Opt. Soc. Am. (Special Issue)* **6**, 490 (1989).
4. V.Z. Kresin, "Proximity Effect and Josephson Tunneling: Application in High T_c Films," *Cryogenics* **29**, 1096 (1989).

Other Publications

5. V.Z. Kresin and S.A. Wolf, "Major Normal and Superconducting Parameters of High- T_c Oxides," *Phys. Rev. B* (in press).
6. V.Z. Kresin and S.A. Wolf, "A Unified Approach to the Description of High- T_c Oxides: Major Normal and Superconducting Parameters," *Physica C* (in press).
7. V.Z. Kresin and H. Morawitz, "The Phonon-Plasmon Mechanism of High T_c ," *Physica C* (in press).
8. V.Z. Kresin, "High T_c Superconductor in an AC Field," *J. Superconductivity* (in press).
9. V.Z. Kresin and H. Morawitz, "Normal and Superconducting Properties of the New High T_c Oxides and

Invited Talks

15. V.Z. Kresin, "Normal and Superconducting Properties of High T_c Oxides," International Conference on High T_c , Mexico City, Mexico, Jan. 1989.
16. V.Z. Kresin, "Major Parameters of High T_c Oxides," Applied Superconductivity Convention, San Francisco, CA, Jan. 1989.
17. V.Z. Kresin, "Origin of High T_c ," Stanford University, Stanford, CA, Apr. 1989.
18. V.Z. Kresin, "Properties of High T_c Films," Conference on Electrochemistry, Los Angeles, CA, May 1989.
19. V.Z. Kresin, "Mechanisms of High T_c ," University of California, Irvine, May 1989.
20. V.Z. Kresin, "Spectroscopy of High T_c Oxides," International Conference on High T_c , Kingston, Ont., July 1989.
21. V.Z. Kresin, "Correlation of Normal and Superconducting Properties in the High T_c Oxides," Institute for Scientific Interchange, Turin, Italy, Sept. 1989; University of Rome, Italy, Sept. 1989; IBM, Zurich, Switzerland, Sept. 1989.
22. V.Z. Kresin, "Proximity Effect," University of Naples, Italy, Oct. 1989.
23. V.Z. Kresin, "Proximity Effect and High T_c ," International Conference (ISS '89), Tsukuba, Japan, Nov. 1989; Special ISTE Seminar, Tokyo, Japan, Nov. 1989.
24. V.Z. Kresin, "Unified Approach to the Physics of High T_c ," University of Tokyo, Nov. 1989; Institute for Molecular Sciences, Okazaki, Japan, Nov. 1989.
25. V.Z. Kresin, "Properties of High T_c Oxides," Varian, Inc., Palo Alto, CA, Dec. 1989.

ELECTRIC POWER RESEARCH INSTITUTE

A Study of Bubble Induced Wear of In-Bed Tubes in Fluidized Bed Combustors*

Alan V. Levy, Investigator

INTRODUCTION

Fluidized bed combustion of coal has many potential advantages over conventional coal burning systems. There are some problems that need to be addressed before fluidized bed combustors (FBCs) become commercially viable. One of these is the high metal wastage of heat exchanger tubes and other internal bed components occurring in many boilers. The present study is concerned with the development of an understanding of a frequently observed and perhaps intrinsic source of wastage in FBCs. This is the wastage of submerged, horizontal, or inclined heat exchanger tubes arising from interactions with bubbles and voids. These bubbles and voids throw dense aggregates of bed materials upward from below to impact the bottom of tubes and cause severe localized three-body abrasive wear. This effect is simulated in a specially designed wear rig by quickly driving a specimen rod downward within a bed of fluidized particles. Through the use of this rig, many aspects of FBC metal wastage have been reproduced, including wear rates, circumferential wear distributions, and wear microstructure.

1. Characterization of Impacts and Their Distribution (Publication 1)

S. MacAdam

The nature of particle impacts and the density at which they occur vary around the circumference of the test rods in a way that is consistent with the flow geometry of particles over the rods and with the steady state metal wastage distribution. The mode of wear is low stress, three-body abrasion. A variety of impact types was observed over the rod surface. These impacts showed all the characteristics of

being caused by particles constrained within a larger aggregate. Only about one-quarter of all contacts were considered to be damaging. Though the remainder were not damaging, they were often very large. The greatest metal damage was caused by impacts with aspect ratios and appearances comparable to those found in impingement erosion. A significant amount of damage also occurred through impacts whose effects on the metal surface resembled those of two-body abrasion. The damage occurred through a combined cutting/plowing process. The actual mechanism of metal loss, however, is thought to be primarily one of segment fracture due to strain accumulation within a highly deformed layer created by repeated particle impacts (low cycle fatigue).

The degree of the damage caused by impacts in this environment is substantially less than that seen in typical erosion or two-body abrasion studies. The time interval between significant impacts in the heavily worn region was approximately four minutes. This is a substantial time that may, under certain conditions, permit the processes of particle dust deposition and oxidation to drastically alter the metal's wear behavior.

2. Influence of Bed Material Properties on Wear (Publication 2)

S. MacAdam

The type of bed material used had a significant effect on the wear rate and distribution about the rod circumference. Under "normal" loading conditions, quartz bed material caused much greater wear than either olivine or silicon carbide. For quartz and olivine, there existed a threshold severity of loading below which essentially no wastage occurred. The threshold for quartz was much lower than that for olivine. Wear caused by silicon carbide was relatively uniform under all severities of loading. The differences were attributable to two factors related to the manner in which bed material comminuted within the fluid environment. One of these factors was the degree to which particles become rounded; the other was the nature of the particle debris formed through comminution and how it was incorporated into the surface of the wear rod.

*This work was supported by the Electric Power Research Institute through Agreement No. RP8000-6.

3. Work in Progress

Elevated Temperature Studies (S. MacAdam)

A new test rig that operates at elevated temperatures characteristic of in-bed tubes in FBCs has been constructed of basically the same design as the room temperature tester. Equipment control, data acquisition, and analysis are accomplished entirely through a computer interface and a program written specifically for the system. Initial tests with this rig have indicated that it has excellent reproducibility and precision in both fluidization and actuation characteristics. The resulting wear behavior can more accurately be related to test parameters, and consequently several subtleties are being revealed. The rig

is currently being used to investigate the combined effects of wear and corrosion.

1989 PUBLICATIONS AND REPORTS

Other Publications

1. S. MacAdam and J. Stringer, "Development of an Actuated Specimen Fluidized Bed Wear Testing Unit," in *Proc. Int. Conf. Wear of Materials*, Denver, CO, Apr. 1989, Vol. 2, p. 689.
2. S. MacAdam, J. Stringer, and A.V. Levy, "A Novel Laboratory Test Procedure for Studying In-Bed Erosion—Design and Some Early Results," in *Proc. 10th Int. Conf. Fluidized Bed Combustion*, San Francisco, CA, Apr. 1989, p. 937.

The Influence of Ion Implantation of Reactive Metals on the High-Temperature Oxidation of Heat-Resistant Alloys*

Alan W. Searcy, Investigator

INTRODUCTION

The addition of reactive elements, such as Y, Hf, and Ce, has a number of beneficial effects on the oxidation behavior of alloys that contain Cr or Al in order to develop a protective oxide scale. For both Cr_2O_3 - and Al_2O_3 -forming alloys, oxide adhesion is greatly improved by thermal cycling. For Cr_2O_3 formers, the rate of oxide growth is diminished above 900°C ; the direction of growth is changed from metal transport out to oxygen transport in; and significantly less Cr is required in the alloy to develop a continuous chromia external scale and to suppress the formation of the base metal oxide. However, treatments that appear to be superficial can also be beneficial. These include ion implantation of the reactive elements, and various methods of depositing oxides of the reactive elements on alloy surfaces. From the point of view of elucidating the mechanism of the "reactive-element effect" (REE), these superficial techniques are particularly interesting and useful. The purpose of this work is to study and compare the nucleation, growth, and adhesion of oxide scales formed on alloys with or without the addition of reactive elements.

1. The Effect of Aluminum as an Alloying Addition or as an Implant on the High-Temperature Oxidation of Ni-25 wt% Cr (Publication 4)

P.Y. Hou and J. Stringer[†]

An important issue in elucidating the mechanism of the REE is whether or not an Al_2O_3 dispersion can show an influence in chromia- and alumina-forming alloys. If so, then any argument that involves a doping effect or any effects due to segregation of the reactive element can be eliminated. In this investigation, the oxidation behaviors of

aluminum-implanted Ni-25Cr and 1 wt% Al-containing Ni-25Cr have been studied at 1000°C and 1100°C in oxygen. As did Y-alloy addition or Y-implantation, 1 wt% Al added to Ni-25Cr prevented nodular formation of Ni-containing oxides, improved the spalling resistance of the scale upon cooling to a similar degree, and eliminated the formation of large voids between the alloy and the scale at the oxidation temperature. However, the Al addition did not alter the growth rate of the Cr_2O_3 scale, nor did it change the growth direction. Al implantation produced no effect even when the maximum concentration and depth of penetration were adjusted to be identical with those of the yttrium in the Y-implanted alloy. These results point out that the spalling resistance of the oxide was unconnected with its growth rate or its growth direction; the modified growth of the REE arose from segregation of reactive elements in the oxide scales, and the process responsible for the transport of Ni out through the Cr_2O_3 is different from the processes responsible for chromium and oxygen transport.

[†]Permanent address: Electric Power Research Institute, Palo Alto, CA 94304.

2. Effect of Internal Oxidation Pretreatments and Si Contamination on Oxide-Scale Growth and Spalling (Publication 2)

P.Y. Hou and J. Stringer[†]

Internal oxidation pretreatments carried out in a quartz capsule with a Rhines pack have often been used to obtain oxide dispersion of reactive elements. However, such heat treatment was found to have a profound effect on the subsequent oxidation behavior of alloys. Specimens of Co-15 wt% Cr, Co-25 wt% Cr, Ni-25 wt% Cr, and Ni-25 wt% Cr-1 wt% Al were tested at 1100°C after preoxidation treatments. Even without the development of internal oxide particles, pretreated binary CoCr and NiCr alloys oxidized with significantly lower rates. Selective oxidation of chromium was observed on the non- Cr_2O_3 -forming Co-base alloys, whereas on the Cr_2O_3 -forming Ni-base alloys, elimination of base-metal oxide, reduction in the Cr_2O_3 growth rate, and better scale adhesion were found. These effects were more apparent with preoxidation temperatures greater than 1000°C and with longer pretreatment times. Contamination of Si from the quartz is believed to be the cause.

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3. Room-Temperature Strains in Cr₂O₃ Scales Formed at Elevated Temperatures on Ni-25 wt% Cr and Y- and Al-Doped Ni-25 wt% Cr (Publication 3)

P.Y. Hou and J. Stringer[†]

Ni-25 wt% Cr, Ni-25 wt% Cr-1 wt% Al, and Ni-25 wt% Cr-0.2 wt% Y alloys were oxidized at 1000°C in O₂ to form Cr₂O₃ scales of similar thickness. After cooling to ambient temperature, the residual strains in these oxide films were measured using x-ray diffraction, and qualitative indications of the interfacial strength were obtained using a microindentation technique. Compressive elastic strains of the order of 0.4% were measured on the Y- and Al-doped alloys. These values agree well with calculated thermal strains that arose from cooling. Only 0.1% compressive elastic strains were observed for the undoped Ni-25Cr alloy. Localized scale buckling and separation from the substrate is believed to have allowed relaxation of the strain in this case. The Y- and Al-doped alloys, on the other hand, have extremely strong scale/alloy interfaces, and therefore were able to retain higher strain levels.

[†]Permanent address: Electric Power Research Institute, Palo Alto, CA 94304.

4. Work in Progress

Study of the effect of reactive elements will continue on Cr₂O₃-forming alloys. The enhanced selective oxidation of Cr in alloys containing reactive elements will be studied in more detail, since Si contamination is now known to have caused some complications in interpreting previous results. The chemistry of the oxide/metal interface will also be studied using surface-analysis techniques to relate it to the adhesion properties of the oxides. Studies on the effect of surface-applied reactive-element oxides and ion-implanted reactive elements on the Al₂O₃-forming FeCrAl alloy has been initiated. Systematic studies in this area will

continue in order to investigate the effect of these superficial treatments on Al₂O₃ scale adhesion.

1989 PUBLICATIONS AND REPORTS

Other Publications

1. J. Stringer and P.Y. Hou, "A Comparison of the Effect of Reactive Metal Alloy Additions, Oxide Dispersions, Ion-implantation and Surface Oxide Coats on High Temperature Oxidation," in *Proc. Symp. on Corrosion and Particle Erosions at High Temperatures*, V. Srinivasan and K. Vedula, Eds., TMS Annual Meeting, Las Vegas, NV, Feb. 27-Mar. 3, 1989, p. 383.

LBL Reports

2. P.Y. Hou and J. Stringer, "Effect of Internal Oxidation Pretreatments and Si Contamination on Oxide-Scale Growth and Spalling," accepted by *Oxid. of Metals*; LBL-27866.
3. P.Y. Hou and J. Stringer, "Room Temperature Strains in Cr₂O₃ Scales Formed at Elevated Temperatures on Ni-25 wt% Cr and Y- and Al-Doped Ni-25 wt% Cr," submitted to *Acta Metall.*; LBL-29413.
4. P.Y. Hou and J. Stringer, "The Effect of Aluminum as an Alloying Addition or as an Implant on the High Temperature Oxidation of Ni-25 wt% Cr," submitted to *Oxid. of Metals*; LBL-28626.

Invited Talks

5. J. Stringer and P.Y. Hou, "A Comparison of the Effect of Reactive Metal Alloy Additions, Oxide Dispersions, Ion-implantation and Surface Oxide Coats on High Temperature Oxidation," Symposium on Corrosion and Particle Erosions at High Temperatures, TMS-AIME Annual Meeting, Las Vegas, NV, Feb. 27-Mar. 2, 1989.
6. P.Y. Hou, "The Reactive Element Effect in High Temperature Oxidation," United Technology Research Center, East Hartford, CT, Sept. 7, 1989.

APPENDIX A

DIVISION PERSONNEL*

1989 Scientific Staff

Investigators	Postdoctoral and Other Scientists	Graduate Students		Participating Guests
Neil Bartlett	R. Hagiwara	W. Casteel S. Mayorga	B. Shen	
Robert Bergman		A. Baranger K. Bharucha E. Burkhardt M. Burn J. Duncan T. Foo D. Glueck	J. Hartwig M. Hostetler D. Klein R. Michaelman R. Simpson P. Walsh E. Wasserman	
Leo Brewer		B. Ebbinghaus J. Kouvetakis	K. Krushwitz S. Leonard	
John Clarke		A. Cleland N. Fan M. Heaney	J. Kingston A. Miklich J. Schmidt	R. Dalven
Marvin Cohen		T. Barbee A. Liu	S. Zhang	A. Garcia
Eugene Commins		K. Abdullah	S. Ross	
Robert Connick	S. Lee			
Didier de Fontaine		A. Berera	P. Huang	M. Kraitichman S. Menon M. Weidenmeier
Lutgard De Jonghe	M. Liu S. Visco	W. Honig		

*Does not include Division Personnel affiliated only with CAM.

Investigators	Postdoctoral and Other Scientists	Graduate Students		Participating Guests
Norman Edelstein	D. Ball	T. Boussie	D. Pichler	H. Amberger
	S. Beshouri	M. Fabiano	R. Rosen	D. Eakin
Richard Andersen	J. Bucher	T. Fanczyk	M. Smith	T. Karpishin
Kenneth Raymond	C. Pippin	L. Gong	S. Stults	S. Konetschny-Rapp
Andrew Streitwieser, Jr.	G. Shalimoff	C. Jenson	L. Uhler	S. Lee
	G. Williams	W. Kot	M. Weydert	B. Lulay
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APPENDIX B

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L. Maio
R. Muller
D. Owen
P. Ruegg
G. Shalimoff

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R. Ellis

Building 72 Building Manager:
M. Moore
(Alternate: E.C. Nelson)

Building 2 Building Manager:
B. Harshman
(Alternate: L. Johnston)

APPENDIX C

LIST OF DIVISIONAL SEMINARS

Chemical Dynamics Seminars

<u>Date</u>	<u>Speaker and Affiliation</u>	<u>Seminar Title</u>
1-23-89	D. Heard, Physical Chemistry Laboratory, Oxford University, Oxford, England	Studies of Atom-Radical Reactions using Time-Resolved Pulsed FTIR Emission Spectroscopy
2-9-89	R. Kosloff, Department of Physical Chemistry, The Hebrew University, Jerusalem, Israel	A Quantum Mechanical Tunneling Mechanism for the Dissociation Dynamics of N ₂ on a Catalytic Metal Surface
2-16-89	Y. Demkov, Department of Theoretical Physics, Leningrad State University, Leningrad, USSR	Pseudo Crossings, the Adiabatic Approximation, and Potential Curves
2-27-89	A. Carrington, Department of Chemistry, The University, Southampton, England	The Hydrogen Molecular Ion
4-10-89	H. Kroto, School of Chemistry, University of Sussex, England	C ₆₀ : The Key to the Structure of Carbon Particles in Space and on Earth
4-11-89	W. Klemperer, Department of Chemistry, Harvard University, Cambridge, MA	Van der Waals Molecules
4-17-89	M. Parrinello, International School for Advanced Physics, Trieste, Italy	A New Method for the Study of Ground States of Fermi Systems
4-28-89	B. Kay, Sandia National Laboratory, Albuquerque, NM	State-to-State Inelastic and Gas-Surface Scattering
5-18-89	J. Vigue, Université de Paris, Laboratoire de Spectroscopie, Paris, France	State Resolved Differential Cross Sections of the F + I ₂ Reaction
6-28-89	G. Meijer, IBM Research Center, San Jose, CA	Pulsed-CW Double Resonance on NO
6-30-89	B. Orr, Department of Chemistry, Macquarie University, Sydney, Australia	Rotationally Resolved Vibrational Energy Transfer in Formaldehyde-d ₂ : Can Molecules Remember?
7-6-89	O.J. Nielsen, Risø National Laboratory, Copenhagen, Denmark	Gas Phase Kinetic Studies at Risø National Laboratory, Denmark

<u>Date</u>	<u>Speaker and Affiliation</u>	<u>Seminar Title</u>
7-10-89	J. Bowman, Department of Chemistry, Emory University, Atlanta, GA	Reduced Dimensionality Reaction Dynamics Study of the Cl + HCl Reaction and ClHCl ⁻ Photodetachment
7-10-89	K.H. Welge, Physics Department, Universität Bielefeld, Federal Republic of Germany	Dynamics of Hydrogen Atom Reactions: New Ways
7-11-89	M. Shapiro, Department of Chemical Physics, Weizman Institute of Science, Rehovot, Israel	The Meaning of Lifetime in Photodissociation Experiments: Is it Necessary to do Femtosecond Experiments?
7-12-89	M.V. Basilevsky, Karpov Institute of Physical Chemistry, Moscow, USSR	Transition State Theory for Dissipative Systems
7-14-89	D. Gerlich, Fakultät für Physik der Universität Freiberg, Federal Republic of Germany	Slow Merged Ions and Molecular Beams: Collision Energies in the eV Range
7-24-89	V. Aquilanti, Department of Chemistry, University of Perugia, Italy	Quantum and Semiclassical Dynamics on Reactive Potential Energy Surfaces
7-31-89	C. Jedrzejek, Institute of Physics, Jagellonian University, Krakow, Poland	Quantum Transport of Electrons through Diffusion: Weak Localization in a Superlattice
8-9-89	I.W.M. Smith, School of Chemistry, University of Birmingham, England	Kinetics and Dynamics of Radical-Radical Reactions
9-7-89	K. Rademann, Department of Chemistry, University of Marburg, Federal Republic of Germany	Metal-Insulator Transition in Mercury Clusters
9-29-89	C.A. Nicolaides, Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Athens, Greece	Structure, Stability, and Highly Exothermic Reactions of Exotic Molecular States
10-12-89	B. Venkataraman, Tata Institute, Bombay, India	Study of Diffusion-Controlled Reactions by Single Photon Fluorescence
11-3-89	J.R. Huber, Physikalisch-Chemisches Institut der Universität Zurich, Switzerland	Energetics, Stereochemistry, and Dynamics of a Photochemical Decay (the Photodissociation of Nitrites)
11-17-89	M. Bulanin, Department of Molecular Spectroscopy, Institute of Physics, Leningrad University, USSR	Electric Properties and Vibrational Dynamics of van der Waals Complexes

Electron Microscopy Seminars

<u>Date</u>	<u>Speaker and Affiliation</u>	<u>Seminar Title</u>
1-18-89	J. Douin, NCEM	The Formation of Twinned Precipitates in Al-Ge Alloys
1-23-89	J.-O. Malm, University of Lund, Sweden	Dynamic Properties of Metal Particles Studied by HREM
2-22-89	M. Stampfer, NCEM	SLEEP—An Interactive Computer Program for Quantification of EELS Data
3-6-89	H. Endoh, Osaka University, Japan	Image Simulation Studies at Osaka University
3-29-89	H. Hashimoto, Okayama University, Japan	Visualization of Atoms in Crystals with Small Movements
4-6-89	A. Petford-Long, University of Oxford, England	The Application of High Resolution Electron Microscopy to the Study of Small Particles
4-27-89	V. Vitek, University of Pennsylvania	Atomistic Structure of Grain Boundaries: Computer Modeling
8-16-89	O. Eibl, Siemens AG, Munich, Federal Republic of Germany	Structure and Defect Structure of High-T _c Superconductors

Other Seminars Hosted

1-17-89	R. Lerner, Scripps Clinic and Research Foundation, La Jolla, CA	Catalytic Antibodies
1-24-89	R. Schrock, Chemistry Department, MIT, Cambridge, MA	Recent Results in Metathesis Chemistry Including Controlled Ring Opening Metathesis Polymerization
1-31-89	D.H.R. Barton, Texas A&M University, College Station	The Invention of Chemical Reactions
2-7-89	D.R. Williams, Indiana University, Bloomington	Studies of Stemonal Alkaloids. Total Synthesis of (+)-Croomine
2-14-89	Y. Kishi, Harvard University, Cambridge, MA	Natural Product Synthesis: Palytoxin
2-21-89	T. Hudlicky, Virginia Polytechnic Institute, Blacksburg	Microbial Transformations and Annulation Techniques in Synthetic Design
2-28-89	D.J. Cram, University of California at Los Angeles	Molecules Within Molecules, Carceranes and Their Prisoners

<u>Date</u>	<u>Speaker and Affiliation</u>	<u>Seminar Title</u>
3-7-89	W.J. Youngs, Case Western Reserve University, Cleveland, OH	Metallocyclines: Synthesis and Conductivity
3-13/15-89	M. Prior, MCSD (Organizer and Co-Chairman)	Workshop on Highly Charged Ions: New Physics and Advanced Techniques
3-14-89	G. Stork, Columbia University, New York	The Temporary Silicon Connection
3-16-89	G. Stork, Columbia University, New York	Advances in Stereo Control—Histo and Ecotoxin Histriocotoxin
3-28-89	L.E. Overman, University of California, Irvine	Palladium-Catalyzed Polyene Cyclizations
4-4-89	S. Krishnamurthy, Eastman Kodak Co., Rochester, NY	Chemistry of Highly Hindered Trialkoxyaluminumhydrides
4-11-89	C. Walsh, Harvard Medical School, Boston, MA	Molecular Studies on Enzyme in Enterbactin Biosynthesis
4-13-89	C. Walsh, Harvard Medical School, Boston, MA	The Dark and Light Sides of Deazaflavin Coenzymes
4-18-89	P. Wender, Stanford University, Stanford, CA	Molecular Aspects of Tumor Progression: Synthetic Pharmacological and Computer Studies
4-25-89	S. Mills, Merck/Sharp/Dohme Research Laboratories	Synthesis of FK 506
4-27-89	A. Hassner, Bar-Ilan University, Israel	Stereoselectivity during Intramolecular Dipolar Cycloadditions
5-2-89	C.P. Casey, University of Wisconsin, Madison	Reactions of Amphiphilic Carbene Complexes with Electrophiles and Nucleophiles
5-9-89	A.L.J. Beckwith, Australian National University, Canberra	The Pursuit of Selectivity in Radical Reactions
5-11-89	A.L.J. Beckwith, Australian National University, Canberra	Kinetic Probes for Radical Structure and Mechanism
5-16-89	E. Negishi, Purdue University, W. Lafayette, IN	Selective Carbon-Carbon Bond Formation Promoted or Catalyzed by a Transition Metal
7-16/21-89	W. Miller, MCSD (Organizer and Chairman)	1989 Conference on the Dynamics of Molecular Collisions, Asilomar, CA
8-89	Y. Lee, MCSD (Organizer)	Workshop on Chemical Dynamics Research Laboratory, LBL
10-25-89	G. Rosenblatt, MCSD (Organizer)	Symposium Honoring Leo Brewer, LBL

APPENDIX D

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*Boldface numbers indicate investigators' main programs.

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