C00-1198-1210

THE SCIENCE OF MATERIALS

Progress Report

July 1, 1977 - June 30, 1978

April 1978

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Materials Research Laboratory
University of Illinois at Urbana-Champaign

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Prepared For

U.S. DEPARTMENT OF ENERGY

UNDER CONTRACT NO. EY-76-C-02-1198

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ABSTRACT

This Progress Report contains a description of the research results of U. S. Department of Energy Contract EY-76-C-02-1198 during the period July 1, 1977 through June 30, 1978.

The program is designed to provide information concerning the basic properties of materials that are important for the development of energy systems and explores novel properties and materials for future applications.

The research program includes studies of the deformation, stress corrosion and fracture of alloys and geologic materials with emphasis on hydrogen embrittlement of metals; the mechanism of heat transfer across interfaces; catalytic properties of surfaces; and erosion of surfaces by fluid suspended particles. The structure of liquids, polymers and disordered solids is under investigation with emphasis on ionic conduction, phase transitions and radiation damage. Ferro- and pyroelectric materials with potential for solar energy applications are under development. The study of optical properties includes the mechanism of luminescence and new semiconductor materials for photovoltaic devices. The electronic properties of crystals is the subject of a continued effort to resolve current problems of magnetic behavior and photon-solid interactions. Specific quantum properties of matter are explored with emphasis on superconductivity, diffusion of hydrogen in metals and the properties of solid helium.

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Materials Research Laboratory
University of Illinois
at Urbana-Champaign

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INTRODUCTION

The Materials Research Laboratory, an interdepartmental unit of the College of Engineering, is organized to facilitate interdisciplinary basic research on the properties of materials. It is affiliated with the School of Chemistry and the Departments of Ceramic Engineering, Electrical Engineering, Geology, Metallurgy and Mining Engineering, and Physics. The Laboratory maintains close working relationships with the Coordinated Science Laboratory, the Materials Engineering Group--Mechanical Properties, and departments of the University.

The primary support of the Laboratory program has been derived from Contract EY-76-C-02-1198 with the U.S. Department of Energy, Grant DMR-76-01058 with the National Science Foundation, and funds of the University of Illinois.

The policies and procedures of the Laboratory have been administered by a Director and Steering Committee consisting of members of the Departments of Chemical Engineering and Chemistry, Ceramic Engineering, Electrical Engineering, Metallurgy and Mining Engineering, and Physics. The Director and Steering Committee are responsible to the Dean of the College of Engineering. They are advised by two committees--an External Advisory Committee of distinguished materials scientists and an Internal Advisory Committee which is chosen by the Laboratory membership. Other committees appointed by the Director supervise the operation of the Central Facilities and Equipment Acquisition.

The present Director of the Laboratory, Professor Robert Maurer, will leave this position April 30, 1978. Professor Colin Peter Flynn of the Department of Physics, a distinguished solid state physicist, will replace

Professor Maurer. Professor Flynn, the author of POINT DEFECTS AND DIFFUSION, Oxford University Press (1972), has a vigorous research program on the electronic structure of surfaces and of alloys. His continuing collaboration with Professor Howard Birnbaum of the Department of Metallurgy and Mining Engineering has been of major value to the MRL-DOE thrust on "Hydrogen in Metals".

Some changes in the administrative structure of the Laboratory will be effected during the summer of 1978 to reflect the program changes that have occurred during the past few years. An organization chart is shown on page 3. The Steering Committee will be replaced by a Program Committee composed of senior members of the Laboratory. A Departmental Liaison Committee will coordinate the Laboratory program with the research of the relevant departments. These changes are designed to improve the choice, operation and evaluation of the Laboratory research and to provide closer cooperation with both the basic and engineering research of the campus.

The DOE supported research program of the Laboratory includes one thrust, "Hydrogen in Metals", a cooperative investigation on the nature of interstitial hydrogen (and helium) in bcc metals, its mobility, and effect on strength and fracture. Related to the research on hydrogen is an investigation of surfaces with emphasis on stress corrosion, fracture, corrosion and erosion. A second aspect of the surface research is the study of the modes of heat transfer across solid-solid and solid-liquid interfaces. A third aspect of the work on surfaces is concerned with the catalytic properties of oxides, transition metal compounds, and commercial platinum catalysts.

Investigations of the structure of polymers, liquids, and disordered solids are in progress which include the topics of superionic conductors, layered compounds, radiation damage and quantum solids. Much of this research is concerned with the complex phase transition behavior of materials. Deformation, plastic flow, and fracture of geophysically important rock materials are associated with this program.

High pressure techniques are used to investigate luminescence mechanisms and energy transfer in solids. Related optical properties research includes the exploration of novel materials for solar photovoltaic devices and the mechanisms of operation of semiconductor diode lasers.

Research on dielectrics emphasizes the growth of new materials and the fabrication of composites with high dielectric constant, high temperature capabilities. Ferro- and pyroelectric materials are being developed for solar energy applications.

Research on superconductors is centered on the effect of magnetic impurities on the superconducting transition temperature and collaboration with the Hydrogen in Metals Thrust concerning the role of dissolved hydrogen on the superconductivity of metals.

The research on oxide systems will be expanded with DOE support by a new member of the Laboratory, Professor William T. Petuskey, who will join the Department of Ceramic Engineering in 1978. Professor Petuskey, who received his Ph.D. from M.I.T., is presently on a postdoctoral appointment in Germany investigating high temperature ceramics with MHD applications.

A major expansion of our characterization of heterogeneous alloys and ceramics, both chemically and structurally, has been permitted through

acquisition of a new analytical electron microscope. New efforts in coal characterization and on ore reduction processes are planned.

The operation of central facilities which support the research program is a primary function of the Laboratory. The major facilities are the Chemical Analysis Facility, the Microstructure Facility, the Machine Shop and the Computer Facility.

The Chemical Analysis Facility employs five professional staff members. Its major instrumentation includes an AEI IM20 ion microprobe, an AEI MS-7 mass spectrograph, a Baird 3 meter emission spectrograph, atomic absorption and flame photometers, and two Auger spectrometers, one of which is a Physical Electronics 544 scanning microprobe.

The Microstructure Facility is staffed by three professional employees. It is instrumented with a JSEM 200 kilovolt transmission electron microscope with STEM and an Oster energy dispersive x-ray spectrometer, an ARL EMX electron microprobe, a scanning electron microscope and an ion milling machine for specimen preparation. In January 1978, a Vacuum Generator 120 kilovolt analytical electron microscope was added to the facility.

The Machine Shop employs eight instrument makers and machinists. It is well equipped for precision instrument construction.

During the past year, the Computer Facility's Sigma 5 system was replaced with a DEC 20-40 system with a 128,000 word memory and 200 megabytes of magnetic disk storage. The new system provides a capability for on line real time data processing. The system is operated by a professional staff member with the assistance of part time student operators.

The minor facilities of the Laboratory include an Optical Laboratory for Raman, infrared and ultraviolet spectroscopy; a Mechanical Test Laboratory

with a Model 810 Materials Test System; a High Temperature Laboratory with two vacuum furnaces; a Toxic Materials Laboratory with special dry box, hood, sink and ventilation; an Accelerator Laboratory with a 3 MeV electron and proton accelerator; a Cryogenic Laboratory with 15 stations for work with liquid helium; and a Material Preparation Laboratory for crystal growth.

In 1978-79 a new X Ray Facility will be created with a 15 KW rotating anode generator. This facility will provide a capability for diffuse x-ray scattering, XAFS, and conventional diffractometry.

Chart of MRL Organization

Terminated Projects

Interstitial Solid Solutions

Carl J. Altstetter, Sc.D., Professor of Physical Metallurgy

Support of this project has been transferred from the U.S. Department of Energy to the National Science Foundation.

Deformation in Reinforced Metals

Marvin Metzger, Ph.D., Professor of Physical Metallurgy

Support of this project has been transferred from the U.S. Department of Energy to the National Science Foundation.

New Projects

Theory of Polymers

Richard J. Gaylord, Ph.D., Assistant Professor of Metallurgical Engineering

Support of this project has been transferred to the U.S. Department of Energy from the National Science Foundation.

Mechanical Properties of Solids

Jon T. Holder, Ph.D., Associate Professor of Geology

Support of this project has been transferred to the U.S. Department of Energy from the National Science Foundation.

Awards and Honors

BIRNBAUM, H. K., Metallurgy

Fellow, New York Academy of Science 1977

DRICKAMER, H. G., Chemical Engineering and Chemistry

American Association for the Advancement of Science (AAAS) Fellowship 1977

MAURER, R. J., Physics

Member, Advisory Committee for Energy, Center for Energy and Environment, University of Puerto Rico, 1977-78

SIMMONS, R. O., Physics

Chairman, Division of Solid State Physics, American Physical Society 1977-78

Member, Publications Committee, Division of Solid State Physics, American Physical Society, 1977-78

Member, Sub-Panel on Users Community, Panel on Research Facilities and Scientific Opportunities in the Use of Low-Energy Neutrons, National Research Council, NAS, Washington, D. C., 1977

Member, AUA Special Committee on the Intense Pulsed Neutron Source, Argonne Universityities Association, 1978-82

Member, Editorial Advisory Board, Physical Review B, 1978-81

Member, Selection Committee, American Physical Society Congressional Fellows Program, 1978

Invited Talks (Calendar Year 1977)

- ALKIRE, R. C. "Electrochemical Engineering," Illinois Institute of Technology, Chicago, IL, February 16, 1977.
- ALKIRE, R. C. "Transport Phenomena in Localized Corrosion," Monsanto Corporate Engineering Center, St. Louis, Missouri, May 23, 1977.
- ALKIRE, R. C. "Distribution of Current in Electrolysis Cells," General Motors Technical Center, Warren, MI, June 2, 1977.
- ALKIRE, R. C. Short Course in Electrochemical Engineering, Brookhaven National Laboratory, Upton, NY, July 11-15, 1977.
- ALKIRE, R. C. "Electroorganic Synthesis," Gulf Oil Chemicals Research Center, Pittsburgh, PA, September 13, 1977.
- ALKIRE, R. C. "Engineering Analysis of Electroplating Systems," Republic Steel Corporate Research Center, Cleveland, OH, October 13, 1977.
- ALKIRE, R. C. "Fundamental Aspects of Electrochemical Engineering," IBM T. J. Watson Research Center, Yorktown Heights, NY, November 17, 1977.
- ANDERSON, A. C. "Kapitza Resistance," Argonne National Laboratory, Argonne, IL, May 4, 1977.
- ANDERSON, A. C. "Low Temperature Properties of Beta-Alumina," Ford Laboratories, Dearborn, MI, June 20, 1977.
- BIRNBAUM, H. K. "Hydrogen Embrittlement Mechanisms," The Technion, Haifa, Israel, June 1977.
- BIRNBAUM, H. K. "Hydrogen in BCC Metals," Sixth International Conference on Internal Friction and Acoustic Attenuation in Solids, Tokyo, Japan, July 6, 1977.
- BIRNBAUM, H. K. "Hydrogen Embrittlement of Solids," National Institute for Metals, Tokyo, Japan, July 1977.
- BIRNBAUM, H. K. "Hydrogen Embrittlement of Solids," Kyoto University, Kyoto, Japan, July 1977.
- BIRNBAUM, H. K. "Hydrogen Mobility in BCC Metals," Tohoku University, Sendai, Japan, July 1977.
- BIRNBAUM, H. K. "The Mechanisms of Hydrogen Related Failures," AIME Meeting, Symposium on Environmentally Related Fracture, Chicago, IL, October 1977.

BIRNBAUM, H. K. "The Mechanisms of Hydrogen Embrittlement," University of Houston, Houston, TX, November 1977.

BIRNBAUM, H. K. "The Mechanisms of Hydrogen Embrittlement," Brookhaven National Laboratory, Upton, NY, December 1977.

DRICKAMER, H. G. "High Pressure on Electronic Structure," Colloquium, IBM, Yorktown Heights, NY, January 1977.

DRICKAMER, H. G. "High Pressure Studies on Luminescence Efficiency," Seminar, University of Karlsruhe, Department of Physical Chemistry, W. Germany, March 1977.

DRICKAMER, H. G. "High Pressure Studies on Luminescence Efficiency," Colloquium, Max Planck Institute for Solid State Physics, Stuttgart, W. Germany, March 1977.

DRICKAMER, H. G. "High Pressure Studies on Optical Phenomena in Electronic Molecules," Plenary Lecture - European High Pressure Conference, Darmstadt, W. Germany, March 1977.

DRICKAMER, H. G. "High Pressure and Electronic Structure," Seminar, Department of Chemistry, University of Darmstadt, W. Germany, March 1977.

DRICKAMER, H. G. "High Pressure Studies of Electronic Phenomena," Bridgman Award Lecture - International Association for Advancement of High Pressure Research and Technology - VI International Meeting, Boulder, CO, July 1977.

DRICKAMER, H. G. "Electronic Transitions at High Pressure," Seminar, Shock Wave Group, Institute for Chemical Physics, Moscow, USSR, September 1977.

DRICKAMER, H. G. "High Pressure Studies on Luminescence Efficiency," Seminar, Institute for Crystallography, Moscow, USSR, September 1977.

DRICKAMER, H. G. "High Pressure Studies of Electronic Phenomena," Colloquium, Institute for High Pressure Physics, Moscow, USSR, September 1977.

DRICKAMER, H. G. "High Pressure Studies on Luminescence Efficiency," Seminar, Institute for Low Temperature Physics, Moscow State University, USSR, October 1977

DRICKAMER, H. G. "High Pressure Studies of Electronic Phenomena," Colloquium, Institute for Chemical Physics, Moscow, USSR, October 1977.

GAYLORD, R. J. "The Amorphous Contribution to the Modulus of a Semi-crystalline Polymer," American Chemical Society Meeting, Symposium on Crystallinity Control and Polymer Mechanics, Chicago, IL, September 1977.

GAYLORD, R. J. "A New Approach to the Deformation of Bulk Polymers," Ford Motor Corporation, Dearborn, MI, August 1977.

GINSBERG, D. M. "Superconductivity Research at the University of Illinois," Duisburg Rheinisch-Westfälische Technische Hochschule, W. Germany, May 2, 1977.

GINSBERG, D. M. "Superconductivity Research at the University of Illinois," University of Cologne, Germany, May 3, 1977.

GINSBERG, D. M. "The Effect of Magnetic Impurities on the Properties of Superconductors," University of Cologne, Germany, May 6, 1977.

GINSBERG, D. M. "The Effect of Magnetic Impurities on the Properties of Superconductors," Karlsruhe Kernforschungsanlage, W. Germany, May 9, 1977.

GINSBERG, D. M. "The Effect of Magnetic Impurities on the Properties of Superconductors," Aachen Rheinisch-Westfälische Technische Hochschule, W. Germany, May 11, 1977.

GINSBERG, D. M. "Breaking Cooper Pairs in Superconductors," Colloquium, City College of the City University of New York, December 14, 1977.

GRANATO, A. V. "Point Defect Interactions with Dislocations," Institut für Kernforschung, Hahn-Meitner Institut, Berlin, Germany, January 10, 1977.

GRANATO, A. V. "Dislocation - Phonon Interactions," Sixth International Conference on Internal Friction and Ultrasonic Attenuation in Solids, Tokyo, Japan, July 7, 1977.

GRANATO, A. V. "Dislocation Inertial Effects in Crystals," Japan Atomic Energy Research Institute, Tokai-mura, Japan, July 11, 1977.

GRANATO, A. V. "Dislocation Inertial Effects in Crystals," The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai, Japan, July 15, 1977.

GRANATO, A. V. "Mechanical Properties of Crystals," Department of Material Physics, Osaka University, Japan, July 18, 1977.

HOLDER, J. "Ultrasonic Studies of Interstitial Impurity Complexes in Electron-Irradiated Aluminum Alloys," Seminar, Institute for Physical Metallurgy, Rhein-Westfahl. Technische Hochschule Aachen, W. Germany, November 28, 1977.

HOLDER, J. "Laboratory Studies of Plastic Flow in Ice Crystals," Colloquium, Institute of Mineralogy, Rhein-Westfahl. Technische Hochschule Aachen, W. Germany, January 12, 1978

JONAS, J. "High Pressure Studies of Dynamic Structure of Liquids," Ippatieff Award Symposium, ACS Meeting, New Orleans, LA, March 1977.

JONAS, J. Lectures on "Magnetic Resonance Spectroscopy at High Pressure," NATO Advanced Study Institute on High Pressure Chemistry, Corfu, Greece, September 1977.

JONAS, J. "Experimental Studies of Molecular Motions in Liquids at High Pressure," Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA, October 1977.

JONAS, J. "High Pressure NMR Studies of Order-Disorder Transitions," Gordon Research Conference on Orientational Disorder in Crystals, Santa Barbara, CA, January 1978.

JONAS, J. "NMR and Raman Studies of Liquids at High Pressure," Department of Chemistry, University of California, Berkeley, CA, January 1978.

KOEHLER, J. S. "Interstitials in Metals," University of Missouri, Columbia, MO, October 1977.

LAZARUS, D. "Superionic Conductors," Physics Colloquium, University of Utah, Salt Lake City, February 1977.

LAZARUS, D. "Superionic Conductors," Physics Colloquium, Brigham Young University, Provo, Utah, February 1977.

LAZARUS, D. "Current Problems in Diffusion," Seminar, CELAM, Gif-sur-Yvette, France, October 1977.

PAYNE, D. A. "Thick Film Ceramic Capacitors with Glass-Bonded Electrodes: Influence of Interfacial Reaction Layers on Dielectric Properties," Canadian Ceramic Society, Quebec City, February 1977.

PAYNE, D. A. "Dielectric Materials for Ceramic Capacitors," American Ceramic Society Electronics Division, Montreal, Canada, October 1977.

PUGH, E. N. "Current Understanding of the Mechanism of SCC in Austenitic Stainless Steels," and "Current Understanding of SCC of Copper Alloys," Golden Gate Welding and Metals Conference, San Francisco, CA, January 1977.

PUGH, E. N. "The Effect of Microstructure on Environmentally-Induced Fracture--an Overview," American Institute of Mining, Metallurgical and Petroleum Engineers (AIME) Annual Meeting, Atlanta, GA, March 1977.

PUGH, E. N. "An Evaluation of Our Current Understanding of Stress-Corrosion Failures," National Association of Corrosion Engineers Research Conference, San Francisco, CA, March 1977.

- PUGH, E. N. with A. J. Bursle, "On the Mechanism of Transgranular SCC," International Conference on Mechanisms of Environment-Sensitive Cracking of Materials, University of Surrey, England, April 1977.
- PUGH, E. N. "The Mechanism of SCC," ARO Workshop on Degradation and Reactivity of Materials, Wrightsville Beach, NC, May 1977.
- PUGH, E. N. "SCC and HE," Keynote Talk - AFOSR-AFML Workshop on Corrosion of Aircraft, St. Augustine, FL, September 1977.
- PUGH, E. N. with A. J. Bursle, "An Evaluation of Current Models for the Propagation of Stress-Corrosion Cracks," AIIME Symposium on Environment-Sensitive Fracture of Engineering Materials," Chicago, IL, October 1977.
- PUGH, E. N. "SCC - A Continuing Practical Problem," American Society of Metals, Sangamon Valley Chapter Meeting, Decatur, IL, November 1977.
- SIMMONS, R. O. "Vacancies in Solid Helium," Symposium on Quantum Fluids and Solids, Sanibel Island, FL, January 1977.
- SIMMONS, R. O. "X-ray Studies of Phase Transitions and Thermal Expansion of Solid Methanes," Gordon Research Conference on Orientational Disorder in Crystals, Santa Barbara, CA, January 1978.
- SLICHTER, C. P. "Probing the Kondo Magnetization Cloud," Colloquium, Department of Physics, Massachusetts Institute of Technology, Cambridge, MA, February 1977.
- SLICHTER, C. P. "Probing the Kondo Magnetization Cloud," Greater Washington Solid State Physics Colloquium, Reiss Science Center, Georgetown University, March 1977.
- SLICHTER, C. P. "The Spin Polarization near Magnetic Atoms in Copper," presented by T. J. Aton, American Physical Society Meeting - Symposium of the Division of Solid State Physics, San Diego, CA, March 1977.
- SLICHTER, C. P. "The Spin Polarization near Magnetic Atoms in Copper," presented by T. J. Aton, 1977 Gordon Conference on Magnetic Resonance, Plymouth, NH, June 1977.
- SLICHTER, C. P. "Satellite NMR - A New Way to Answer Some Old Questions about Magnetism," Washington University, St. Louis, MO, November 1977.
- SLICHTER, C. P. "Satellite NMR - A New Way to Answer Some Old Questions about Magnetism," University of British Columbia, Vancouver, Canada, November 1977.
- SLICHTER, C. P. "Satellite NMR - A New Way to Answer Some Old Questions about Magnetism," University of Texas, Austin, TX, December 1977.

STAPLETON, H. J. "Spin-Lattice Relaxation - A New Probe of Hemoproteins," Joint Chemistry and Solid State Physics Divisions, Oak Ridge National Laboratory, Oak Ridge, TN, March 1977.

STAPLETON, H. J. "Spin-Lattice Relaxation - A New Probe of Hemoproteins," Physics Department, University of Alabama, Birmingham, April 1977.

Leaves of Absence

HOLDER, J. T., Geology
July 1977 - January 1978
Institut für Allgemeine Metallkunde und Metallphysik
Rhein.-West. Technische Hochschule Aachen, West Germany

WILLIAMS, W. S., Ceramic Engineering and Physics
1977-78
Section Head, Metallurgy and Materials Section, Division of
Materials Research, National Science Foundation, Washington, D. C.

Travel

Professor H. K. Birnbaum, Department of Metallurgy and Mining Engineering, attended the Sixth International Conference on Internal Friction and Acoustic Attenuation in Solids held in Tokyo, Japan on July 4-7, 1977. Two papers were presented: an invited review paper on "Hydrogen in BCC Metals" and a presentation of recent scientific results "Acoustic Studies of Hydride Phase Transitions". Professor Birnbaum presented technical papers and visited the Institute for Solid State Physics Research, Tokyo University, Chuo University, National Research Institute for Metals, Tohoku University, Kyoto University and Osaka University. The total cost to the U. S. Department of Energy contract was \$1,067.

Visiting Staff

Dr. B. S. Chandrasekhar, Department of Physics, Case Western Reserve, Cleveland, Ohio, is a Visiting Professor of Physics interacting with the low temperature group, July 1, 1977 through May 30, 1978.

Dr. Robert Franks, Professor of Physics at Augustana College, was a Visiting Professor of Metallurgy, June and July of 1977, interacting with Professors H. K. Birnbaum and C. A. Wert on trapping effects in diffusion of hydrogen.

Professor George S. Handler, Department of Chemistry, University of Georgia, Athens, was a visitor July 1 through August 15, 1977. He is an expert on local density techniques for electronic structure properties and consulted with Professor A. B. Kunz and his group on this topic.

Dr. Michael W. Klein, Department of Physics, Bar-ilan University, Ramat-Gan, Israel, is a Visiting Professor of Physics working with Professors A. C. Anderson and M. V. Klein, August 21, 1977 through May 20, 1978.

Dr. E. Schempp, Visiting Associate Professor of Physics, is working with Professor T. L. Brown of the Department of Chemistry, January 6 through May 20, 1978.

Professor T. W. Sigmon of the Department of Electrical Engineering, Oregon State University, Corvallis, collaborated with Professor C. A. Evans on the role of impurities in controlling the growth of silicon epitaxial layers and the electrical properties of electric materials, June 20 through August 1, 1977.

Professor R. B. Weil, Department of Physics, Technion-Israel Institute of Technology, Haifa, is a Visiting Associate Professor of Physics, August 21, 1977 through May 20, 1978, working with Professor D. Lazarus.

Other Visitors

Dr. C. W. Frank, Department of Chemical Engineering, Stanford University, Palo Alto, CA visited the Laboratory to consult with Professor H. G. Drickamer and give a seminar, January 27, 1977.

Dr. James S. Kane, Director, Division of Physical Research, U.S. Energy Research and Development Administration, Washington, D. C., visited the Laboratory on February 23, 1977.

Dr. Ruy de Azambuja Villanova, Analytical Laboratory Chief, Acos Finos Piratini S/A, Brazil, visited the Laboratory to discuss tendencies of the new analytical instruments and new approaches in the analytical field, March 2-5, 1977.

Dr. A. G. Kachaturyan, Visiting Professor, University of California, Berkeley, consulted with Professor C. M. Wayman and his group on pre-transformation phenomena, discussed elastic calculations with Professor H. E. Cook, and gave a seminar, April 12-14, 1977.

Mr. Lee E. Tanner, Materials Research Center, Allied Chemical Corporation, Morristown, NJ was a visiting seminar guest April 13-15, 1977.

Professor Fritz Luty, Department of Physics, University of Utah, Salt Lake City, visited several members of the Laboratory and gave a seminar, April 28-29, 1977.

Professor Walter Stockmayer, Department of Chemistry, Dartmouth College, Hanover, NH visited H. G. Drickamer's laboratories and gave a seminar, May 2-3, 1977.

Dr. Bruce N. Colby, Monrovia, CA visited the Laboratory to consult with Professor C. A. Evans, Jr., on ion probe analysis of biological materials, May 18-19, 1977.

Professor Carlo Jacoboni of Instituto di Fisica dell Universita of Modena, Italy, consulted with several members of the Laboratory on Monte Carlo calculations for high-field transport in semiconductors, June 21, 1977.

Professor Meir Weger, Recah Institute of Physics, Hebrew University, Jerusalem, Israel, visited the Laboratory to consult with Professor Robert Maurer, Director of the Laboratory, July 11, 1977.

Professor T. Skoskiewicz, Polska Akademia Nauk, Institute Chemii Fizycznej, Warszawa, Kasprzaka, Poland, visited the Laboratory and A. C. Anderson's group, July 25-26, 1977.

Dr. P. R. Bhowal, Department of Metallurgy, Institute of Materials Science, University of Connecticut, Storrs, visited the Laboratory to consult with Professor M. Metzger, August 1-8, 1977.

Professor Z. Weiss of the University of Puerto Rico visited the Laboratory and consulted with Director Maurer, Professors Payne and Wirtz, August 15-19, 1977.

Professor G. Vogl, H. Meitner Institut, Berlin, visited the A. V. Granato group and gave a seminar on "Radiation Damage Studies with Mössbauer Spectroscopy," September 13, 1977.

Dr. Michel Boudart, Department of Chemical Engineering, Stanford University, visited with H. G. Drickamer and gave a seminar, September 13-14, 1977.

Dr. H. Kanzaki, Institute of Solid State Physics, University of Tokyo, Japan, visited the Laboratory to discuss with Professor F. C. Brown the recent work in Japan on excited states in insulating crystals.

Professor Hellmut Fritzsche, Director, The James Franck Institute, University of Chicago, visited the Laboratory and was the speaker for the joint Physics-MRL Seminar, November 18, 1977.

Dr. Floyd Humphrey, Division of Applied Physics, California Institute of Technology, Pasadena, CA visited the Laboratory for consultations on magnetic materials and gave a colloquium talk, November 17-18, 1977.

Professor Donald R. Beck, Theoretical Chemistry Institute, National Hellenic Research Foundation, Athens, Greece, visited the Laboratory to discuss explicit correlation techniques in molecular systems with Professor A. B. Kunz, January 6, 1978.

Seminars (Calendar Year 1977)

Physics-MRL Solid State Seminar

Atomic Delocalization, Mobility, and Ordering in Solids

Professor C. P. Flynn, Physics, Department, University of Illinois
at Urbana-Champaign

January 21, 1977

Chemical Engineering-MRL Seminar

Luminescence Studies in Polymers

Dr. Curtis W. Frank, Department of Chemical Engineering,
Stanford University, Stanford, CA

January 27, 1977

Special Seminar

Surface and Interface Studies Using Synchrotron Radiation

Dr. R. Bachrach, Xerox Palo Alto Research Center, Palo Alto, CA

March 28, 1977

Special Seminar

Elastic Energy and Morphology of Two-Phase Mixtures

Professor A. G. Chachaturyan, University of California at Berkeley

April 12, 1977

Physics-Metallurgy-MRL Seminar

Metallic Glasses and Their Properties

Dr. L. E. Tanner, Allied Chemical Corporation, Materials Research
Center, Morristown, NJ

April 15, 1977

Physics-MRL Solid State Seminar

Evolution of Molecular Order and Phase-Transitions in Crystals

Professor Fritz Lüty, Physics Department, University of Utah, Salt Lake City

April 29, 1977

Physical Chemistry-ACS-MRL Seminar

Some Aspects of Chain Molecule Dynamics

Professor Walter Stockmayer, Dartmouth College, Hanover, NH

May 3, 1977

Special Seminar

Electronic Conductivity in Cu-Ga Alloys

Dr. Edger Lüscher, Physik Department der Technischen Universität München

May 16, 1977

Special Seminar

First Order Phase Transitions in Magnetism

Professor I. E. Dzyaloschinskii, Landau Institute of Physics, Academy
of Sciences, Moscow, USSR

May 17, 1977

Special Seminar

Pinning of Fröhlich's Wave and Solitons in One-Dimensional Systems
 Professor I. E. Dzyaloshinskii, Landau Institute of Physics, Academy
 of Sciences, Moscow, USSR
 May 19, 1977

MRL-Solid State Seminar

Light Emission via Inelastic Tunneling
 Dr. John Lambe, Ford Motor Co. Research Labs, Dearborn, MI
 May 20, 1977

Special Seminar

The Generalized Density Matrix: A New Approach to the Description
 of Collective Excitations
 Professor S. T. Beliaev, University of Novosibirsk, Novosibirsk, USSR
 May 24, 1977

Special Physics-MRL Solid State Seminar

Significant Differences Between Hartree-Fock and Local Exchange
 Energy Bands for TiO
 Dr. D. Jennison, Department of Physics, University of Illinois
 at Urbana-Champaign
 May 25, 1977

Informal Seminar

Recrystallization of Amorphous Si Layers Created by Self-Ion
 Implantation on Single Crystal Substrates
 Dr. T. W. Sigmon, Oregon State University, Corvallis
 June 24, 1977

Chemistry-Physics-MRL Seminar

Thermodynamics of Melting of Common Substances
 S. M. Stishov, Institute for Crystallography, Moscow, USSR
 July 8, 1977

Electron-Hole Droplet Seminar

July 8, 1977
 Biexcitons in Stressed Silicon
 Dr. Vladislav Timofeev, Inst. Sol. St. Physics, Chernojolovka, Moscow

Phase Diagram in the Critical Region: Ge

Professor M. B. Salamon, Department of Physics, University of
 Illinois at Urbana-Champaign

EHD in Ge under Uniform $\langle 111 \rangle$ Stress

Dr. B. Feldman, University of Missouri, and Dr. G. D. Wong, Northwestern

Interaction of EHD with Stationary and Alternating Magnetic Fields
 Ya. Pokrovskii, Inst. of Radioengineering, USSR

Imaging of EHD's

Professor J. P. Wolfe, Department of Physics, University of
 Illinois at Urbana-Champaign

Special Seminar

Silver Halide Surface

Dr. Jack Beutel, Senior Scientist, DuPont

July 18, 1977

Special Seminar

Work on Metal-Hydrogen Systems in Poland

Professor T. Skoskiewicz, Polska Akademia Nauk, Institute Chemii

Fizycznych, Warszawa, Kashprzaka, Poland

July 25, 1977

ACS-MRL Seminar

Catalysis by Metals and Alloys

Dr. Michel Boudart, Stanford University, Stanford, CA

September 13, 1977

Physical Chemistry-MRL

Molecular and Electronic Structure Via Nuclear Spin Dynamics:

Spinors, Organic Solids, and Ionic Conductors

Dr. Robert W. Vaughan, California Institute of Technology, Pasadena, CA

October 26, 1977

MRL-Physics Colloquium

Magnetic Bubble Dynamics as Seen by High Speed Photography

Professor F. B. Humphrey, California Institute of Technology, Pasadena, CA

November 17, 1977

Physics-MRL Seminar

The Nature of Localized States in Amorphous Semiconductors

Professor H. Fritzsche, Department of Physics, University of Chicago

November 18, 1977

Special Seminar

Neutron Scattering Studies of Transition Metal Alloys

Dr. Y. Ishikawa, Tohoku University, Japan

November 18, 1977

PROJECT TITLES AND PRINCIPAL INVESTIGATORS

METALLURGY AND CERAMICS

AK-01-02-01-1 Structure of Materials

Localized Corrosion of Passive Metals

Richard C. Alkire, Ph.D., Professor of Chemical Engineering

Theory of Polymers

Richard J. Gaylord, Ph.D., Assistant Professor of Metallurgical Engineering

Dynamic Structure of Supercritical Dense Water and Aqueous Electrolyte Solutions

Jiri Jonas, Ph.D., Professor of Physical and Analytical Chemistry

AK-01-02-01-2 Mechanical Properties

Hydrogen Behavior in BCC Metals

Howard K. Birnbaum, Ph.D., Professor of Physical Metallurgy

Characterization of Compounds and Alloys

Hamish L. Fraser, Ph.D., Assistant Professor of Metallurgy, and
Charles A. Wert, Ph.D., Professor of Physical Metallurgy

Mechanism of Stress-Corrosion Cracking: Propagation Studies

E. Neville Pugh, Ph.D., Professor of Metallurgical Engineering

AK-01-02-01-3 Physical Properties

Mechanical Properties of Solids

Jon T. Holder, Ph.D., Associate Professor of Geology

Dielectric Solids

David A. Payne, Ph.D., Assistant Professor of Ceramic Engineering

Nuclear Magnetic Resonance Studies of Metals and Polymers

Theodore J. Rowland, Professor

Electron Paramagnetic Resonance Studies on Fast Ionic Conductors and on
Catalytically Active Oxide Surfaces

Harvey J. Stapleton, Ph.D., Professor of Physics

Oxide Catalysts

Gerald P. Wirtz, Ph.D., Associate Professor of Ceramic Engineering

SOLID STATE PHYSICS

AK-01-02-02-2 Experimental Research

Low Temperature Studies of Defects in Solids

Ansel C. Anderson, Ph.D., Professor of Physics

Response of Solids to Electromagnetic Radiation

John D. Dow, Ph.D., Professor of Physics

Use of Very High Pressure to Investigate the Structure of Matter

Harry G. Drickamer, Ph.D., Professor of Physical Chemistry and
Chemical Engineering

Impurities in Superconductors

Donald M. Ginsberg, Ph.D., Professor of Physics

Ultrasonic Studies of the Structure of Matter

Andrew V. Granato, Ph.D., Professor of Physics

Defect Properties of Solids

David Lazarus, Ph.D., Professor of Physics

Properties of Crystalline Condensed Gases

Ralph O. Simmons, Ph.D., Professor of Physics

Nuclear Magnetic Resonance in Solids

Charles P. Slichter, Ph.D., Professor of Physics

Physics of Refractory Materials

Wendell S. Williams, Ph.D., Professor of Ceramic Engineering, and
Bioengineering

AK-01-02-02-4 Particle-Solid Interactions

Radiation Damage in Solids

James S. Koehler, Ph.D., Professor of Physics

SUMMARY METALLURGY AND CERAMICS

AK-01-02-01-1 Structure of Materials

The primary topics of investigation are:

- (a) The corrosion and erosion of surfaces during fluid flow
- (b) The structure of polymers and liquids.

The focus of the corrosion-erosion research is the mechanism of rupture of passive films on metals by particle impact and the electrochemical processes which control repassivation of the damaged surface or propagate the damage. The examination of micro-structural surface damage by controlled particle impact (ball bearings) and scouring by glass beads carried by fluids in flow cells is proposed. Localized metal loss will be directly measured and the formation of passive layers as a function of fluid flow followed by ellipsometry. Electrochemical techniques will be used to determine the mechanism of repassivation. The role of salt films in repassivation after disruption will be examined as will the mechanism of crevice corrosion. This research of R. Alkire is carried out in cooperation with the stress corrosion and fracture research of E. N. Pugh and H. Birnbaum.

Research on liquids of J. Jonas will concentrate on the dynamic structure of supercritical compressed water and electrolytes. High pressure, NMR, and Raman techniques will be used to measure self-diffusion coefficients, hydration, ion pairing, and hydrogen bonding with continuing attention to transport properties and the feasibility of isotope separation systems.

Exploratory work will be carried out using Raman and NMR techniques on prefreezing phenomena in polar liquids, the structure of molten salts, and the mobility of fluorine ions in the superionic conductors, CaF_2 . The rate of phase transformation (order-disorder) in organic solids will be investigated.

Proton relaxation times will be measured in polymers to reveal the details of chain entanglement. The experimental polymer studies of Jonas will complement the theoretical research of R. Gaylord on polymer chain entanglement and chain interactions, the effect of wall constraints, and stress-strain relations during cyclic loading.

AK-01-02-01-2 Mechanical Properties

The "Hydrogen Metals" thrust which is centered on the investigations of H. Birnbaum will be concerned with the development and refinement of the delocalized quantum model of interstitial hydrogen in bcc metals. The possible persistence of quantum effects on diffusion above 100 K will be investigated. Trapping of hydrogen by other

impurities continues to be an important subject for study. The nitrogen-hydrogen defect will be characterized and compared with the now thoroughly characterized oxygen-hydrogen defect. In cooperation with Argonne and Brookhaven, neutron scattering experiments are planned to reveal the relationship between phonon modes, brittleness and fracture.

The mechanism of hydrogen entry into niobium and nickel (examples of metals with coherent and nonprotective oxide films) will be studied by Auger and Raman techniques with examination of the effect of H_2S , SO_2 and H_2O on entry.

Crack tip processes during fracture will be investigated by x-ray examination of the stress field and plastic deformation at slowly propagating cracks.

Hydrogen embrittlement appears to be responsible for a type of stress corrosion cracking in many alloys which fail by brittle mechanical fracture. Evidence will continue to be sought for the relative importance of this mode of failure and an alternative mode of the dissolution type with film rupture. Experiments will continue to detect hydride on surface of cracks by electron and x-ray diffraction. New emphasis will be placed on the relation of passivation to the dissolution type of stress corrosion cracking in coordination with the corrosion-erosion studies of R. Alkire. The emphasis in the stress corrosion research is on the copper-zinc and titanium aluminum alloys of engineering importance. This work of E. N. Pugh in association with the related efforts of H. Birnbaum, H. Fraser, R. Alkire, and C. Altstetter constitutes a developing thrust in the area of environmentally-induced fracture.

A major effort is planned by H. Fraser and C. Wert on the development of techniques for the characterization on a fine scale of oxides, nitrides and carbides. The program is based on a new VG HB5 analytical electron microscope with an energy loss spectrometer for light element analysis on a scale of the order of 30 Angstroms. Although hydrogen cannot be directly observed, it is hoped that its analysis will be possible through its effect on the plasmon loss peaks of alloys. Two new directions of research are planned. The first is a characterization of coals for which a major collection of representative samples is available from the Illinois Geological Survey. The second new direction is the investigation of the sequential processes involved in reduction of ores with characterization of the intermediate products.

AK-01-02-01-3 Physical Properties of Materials

A major fraction of the research of this group is concentrated on the properties of oxide systems of importance for solar energy, catalytic, and fuel cell applications. Properties of geologic materials are under investigation because of their relevance to energy utilization

and nuclear waste disposal. Exploratory work is in progress on novel organic semiconductors with potential applications to solar photovoltaic cells. Because of the applicability of the available techniques, there is cooperation with the "Hydrogen in Metals" thrust with respect to hydrogen diffusion in the bcc metals.

A primary thrust of the oxide research is the relation between microstructure and dielectric behavior of ceramic materials. A major goal is the optimization of properties by use of polyphasic systems. Materials to be investigated include Bi_2WO_6 , a layered compound; $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ a pyroelectric from which glasses are formed by splat cooling; BaTiO_3 , a candidate for thermal sensors and fuel cell electrodes; and $\text{BaTiO}_3 - \text{Pb}_5\text{Ge}_3\text{O}_{11}$ for energy storage systems. The past emphasis on the development of crystal growth techniques and development of oriented microstructures for maximum electromechanical response will be continued. The role of grain and phase boundaries in determining dielectric response will be investigated. The study of the lanthanum-cobalt-oxygen system, with potential applications in high temperature coal gas fuel cells, will be extended to include the investigation of oxygen chemisorption. This research effort of D. Payne, G. Wirtz and W. Petusky will cooperate with related work at the DOE Center for Energy and Environment at Puerto Rico. H. Stapleton will determine by EPR techniques the nature of catalytically active sites on the surfaces of rare earth oxides like Tb_2O_3 and Lu_2O_3 which are catalysts for hydrogen and oxygen reactions. These same techniques will be applied to the determination of the location of the mobile cations in the superconductor beta alumina in cooperation with the high pressure studies of these materials by D. Lazarus.

Exploratory work will be conducted on the electrical properties of novel pseudo one dimensional organic semiconductors, related to TTF-TCNQ, to determine their potential applicability to solar photovoltaic cells and the same NMR techniques of T. Rowland are used for the study of trapping of hydrogen by interstitial impurities in bcc metals in cooperation with the "Hydrogen in Metals" thrust. Theoretical input to this work is provided by A. B. Kunz.

J. Holder will determine rock deformation mechanisms by ultrasonic and acoustic emission techniques. Of particular interest will be the anomalous increase in strength of limestone with temperature and the relative importance of chemical and mechanical processes for increase in hydrothermal porosity in limestone-fluid systems under high temperature and pressure--topics relevant to nuclear waste disposal. The investigation of plastic flow mechanisms and structure of ice will continue. This study involves collaboration with A. Granato and cooperation with the U.S. Army Cold Regions Research Laboratory. The rock deformation research is carried out with the cooperation of F. Donath of the Geology Department and there is a continuing interaction with E. N. Pugh (Metallurgy) and F. V. Lawrence (Civil Engineering) who use similar acoustic emission techniques.

AK-01-02-01-1 Structure of MaterialsLocalized Corrosion of Passive Metals

Principal Investigator: Richard C. Alkire, Ph.D.
Professor of Chemical Engineering

Supporting Agency: U. S. Department of Energy

Senior Staff: Richard C. Alkire, Professor
Chio Ling Wang, Research Associate

Junior Staff: Lee Warren Wiechmann, Research Assistant
David W. Siitari, Teaching Assistant

Object: All structural metals are chemically unstable and tend to oxidize spontaneously. In some cases, however, the oxidation of the metal leads to formation of a surface film which is protective and which thereby acts to reduce the oxidation (corrosion) rate to within acceptable limits. Under adverse situations, however, protective films may be damaged so that the substrate metal is thereby exposed to corrosion. In this project, we are interested in the nature of disturbances which create loss of metal passivity, and in the nature of ensuing processes which lead either to continuance of corrosion or to repassivation.

Typical disturbances which create loss of passivity include high fluid velocity, particle impaction or cavitation as in erosion corrosion; generation of new surfaces as in stress corrosion cracking; non-uniform mass transport as in differential aeration; and surface inhomogeneities as represented by foreign inclusions. After birth of local corrosion activity, the subsequent life and death processes are often controlled by transport processes in the electrolytic solution phase. Many features of localized corrosion processes can be clarified by examining the consequences of transport-controlled flow of current between local anodic and cathodic regions along the corroding surface.

Modeling of corrosion processes is included as an integral part of our experimental program. Therefore, our program provides strategies for attacking a wide variety of corrosion problems which exceed the specific issues we are currently investigating. Our modeling approach provides a conceptual framework for determining scale-up parameters, for analyzing data from complex experiments, for testing hypotheses of behavior, and for predicting system behavior from knowledge of system parameters.

Both experimental and theoretical methods are used in our investigation. One experimental method is to disturb a passive electrode and then follow the response by simultaneous electrical and optical measurement, including ellipsometry. A second experimental method is to section the electrode into parts, each insulated from another but connected externally by zero-resistance operational amplifier circuits; the flow of electrical current between sections is thereby measured and can be related to the distribution of anodic and

cathodic processes along the electrode assembly. Theoretical methods of transport phenomena are used to model salient features of corrosion systems: Diffusion and migration of species, fluid advection, multiple electrochemical reactions, precipitation of insoluble products, kinetics of charge-transfer processes, ohmic resistance between anode and cathode and cell geometry.

In many industrial situations, the design of process equipment leads to adverse conditions under which subsequent corrosion protection is difficult. An improved understanding of corrosion processes, coupled with proper chemical engineering design methods, is needed. By careful control of fluid flow conditions, for example, it is entirely possible to use carbon steel to contain highly corrosive materials. In the long range, the integration of understanding between chemical engineering and materials science would permit savings of both materials and capital.

Results FY78:

Most Significant Accomplishments: In systems where erosive wear is inevitable, it is important to minimize additional metal loss owing to corrosion. Our development of quantitative methods for experimental study permit controlled variation of corrosion and erosion parameters and will eventually lead to modeling capabilities. Therefore, the results of our program are important since they are leading to a quantitative basis for predicting flow conditions under which sustained corrosive attack cannot occur.

During erosion corrosion, virgin metal surfaces are created and a sequence of electrochemical processes then occurs which includes metal dissolution and formation of a passive oxide film. Using iron electrodes in acidic solution, we have simulated single impaction events by an electrochemical method, which depassivates the metal and then induces repassivation. During early stages of repassivation, it was found that the metal dissolution rate is so large that solubility limits are exceeded and a metal-salt film precipitates. By using an ellipsometer to monitor transient surface processes during repassivation, we have demonstrated that, under sufficiently vigorous agitation, precipitation of a salt film does not occur and repassivation does not take place. That is, for iron in sulfuric acid, the existence of a salt film is a necessary precursor to the re-establishment of a protective passive oxide.

In related work, we have developed electrolysis cells in which the fluid mechanics are well-characterized; these include rotating disk, rotating cylinder and stagnation jet cells. For iron in sulfuric acid, we have found a dramatic dependence of repassivation rate upon flow conditions. A theoretical treatment has been developed for mass transfer aspects of metal repassivation in the presence of uniform flow fields.

Other Results: In studies on crevice corrosion, development of experimental procedures has continued for monitoring variation of pH reaction rate, and

electrical potential along the interior of micro-fissures. Studies have been conducted on Al in NaCl, and Fe in chloride, bicarbonate, dichromate and sulfate electrolytes. The aluminum system provides the most reproducible results and has been chosen for closer study in FY79. To date, all results have been obtained without external energization of the corrosion system; that is, we have concentrated efforts on the "natural" processes which lead to crevice corrosion over a period of time. The experiments are difficult to perform, but are leading to an intuitive understanding of the transient processes which occur during initiation of crevice corrosion. These results will be important in the development of a theoretical model of the process. The model, to be completed during FY78, will be the subject of further study during FY79; prior to May 1977, our crevice corrosion work had received the support of NSF-DMR to whom a request for renewed support has been directed.

In a separately funded study (NSF-ENG) we have developed and demonstrated a new method for calculating shape changes owing to electrochemical dissolution or deposition. The method involves finite element numerical calculations. The method is now available for application to shape-change events which accompany localized corrosion.

Results Expected FY79: In the area of repassivation and salt film phenomena, we plan to evaluate a wide range of chemical systems with our method of controlled potential-jump with simultaneous observation by ellipsometry. In particular, we would seek to determine those conditions under which salt films play a role in metal repassivation. We would investigate why different effects seem to control the repassivation behavior of different metals. For example, hypotheses have included concentration of metal ions in Fe systems (diffusion), pH changes in Cr systems (hydrolysis and migration effects), and local concentration of anions in Ni systems (migration effects). In addition, we would be in a position to examine metals which dissolve to form insoluble surface films (Pb, Ag) and/or complex ions in solution (Au, Cu, Hg). The foregoing exploratory program will identify systems suitable for more thorough study, and will provide a strong intuitive basis for improving current theoretical models which include only metal-ion diffusion effects.

We feel that fundamental studies on erosion-corrosion would be more easily interpreted if the complexities of particle impaction processes could be separated from the complexities of surface repassivation processes. The highly sophisticated flow cells developed in FY78 will be integrated into the present ellipsometer system in order to permit observation of the surface repassivation during hydrodynamic flow. In this manner, we will be able to separate transient surface processes from other transient processes involving, for example, convective mass transport. Further, we would expand our acquisition of fundamental information by developing the capability of direct measurement of localized metal loss with use of a surface profile measuring device. These data would be compared with Faradaic dissolution calculated from measurements of electrical current. By these experiments, a more thorough understanding of flow effects on repassivation will be achieved, and will serve as a basis for theoretical work in FY80. In addition, development

of the above flow-ellipsometer cell will enable us to address an expanded range of experimental research topics in FY80.

A completely new line of flow cells will be developed for introducing controlled particle impaction on to passive electrodes in order to move further toward actual erosion-corrosion configurations. We anticipate that understanding of fundamental aspects will be best achieved through study of single impaction events, for example, by firing individual ball bearings at the electrode surface. Comparison of microstructure and surface damage under corrosive and noncorrosive conditions will be made. Direct measurement of surface profile following impaction-corrosion will be made in order to compare metal loss by erosion and by electrochemical dissolution. In addition, other methods of continuous erosion may be evaluated, such as scouring with electrolytes containing glass beads; although such methods are more typical of field situations, they lead to far less useful information.

Investigations on crevice corrosion would continue, although we may develop alternative funding through NSF-DMR. In any case, we plan to move beyond our current investigation of "natural" corrosion processes, and study the response of a crevice to various conditions of anodic and cathodic protection. The metal dissolution rate along our segmented crevices will be measured directly with use of a profile recording device. Theoretical work from FY78 will be directly applicable to these new aspects of experimental work.

Results Expected FY80: We anticipate two broad areas of investigation within erosion corrosion. In the first, the flow/ellipsometer cell would be employed to investigate the various chemical systems identified in FY79. These studies are expected to lead to a more comprehensive theoretical treatment of flow effects on metal repassivation. In addition, we would build up knowledge of which systems do not exhibit flow dependence, and would thereby be in an improved position to broaden our current perspective on repassivation processes. In the second area, controlled impaction studies would be pursued to gain appreciation of the manner by which the corrosive environment influences impaction damage. Efforts would be made to incorporate mechanical properties of the substrate into the overall perspective. For example, comparison between low-angle and high-angle impaction-corrosion could be made for ductile and brittle substrates. In general, the program would move toward expanding beyond its present constraints of electrochemistry and mass transport, into the area of fracture mechanics.

It would be attractive to expand repassivation studies to investigate surfaces which experience variation in mass transfer rate from place to place. The central question is whether acquisition of passivity at one point of the surface will spread laterally into well-stirred regions that would not otherwise passivate. If surfaces are indeed able to passivate by lateral communication, then there may be a critical size of impaction damage below which permanent loss of passivation would not occur.

The availability of sophisticated flow cells would make it possible to broaden our study of flow effects in corrosion. In particular, we could turn to flow

effects on corrosion inhibition by adsorbed organic species. Under high shear stress, the adsorbed surface layer of inhibitor species may be disrupted, creating a local "patch" of bare metal. Resultant corrosive attack would depend upon the rate of re-inhibition by adsorption from the flowing fluid. Since inhibitors are usually present in micromolar quantities, the re-inhibition process would be largely mass transfer controlled. Our current techniques could easily be expanded to study this new repair process.

In other (non-MRL) research, we are developing and applying strategies for modeling complex electrochemical systems. Corrosion systems constitute an important class of application of these methods. The crevice corrosion problem is particularly suitable for study owing to its simple geometry. Therefore, we plan to investigate the response of corroding crevices to unsteady state upsets. Experiments will be conducted with the fully instrumented artificial crevices perfected in FY78-79. Theoretical work will be based on our previous models. We would study periodic cathodic and anodic protection of crevices, and timewise variation of solution composition outside the crevice.

Relationship to Other Projects: The likelihood of duplication between this program and others is small since there are so few centers where the study of corrosion is combined with electrochemical engineering. There are five DOE programs on erosion (LBL, ORNL, ANL, San-A, Illinois) of which only two include corrosion, and only ours is in liquid electrolytes. We pursue regular contacts with other laboratories in assuring conflict-free programs.

In off-campus endeavors, we are heavily involved with Dr. Theodore R. Beck in stress corrosion cracking work carried out at Electrochemical Technology Corp., Seattle. His work on repassivation kinetics, supported by ONR and AFOSR, has established mass transfer control processes which are currently being pursued in our erosion-corrosion work at Illinois. We are also collaborating with Dr. Bart Ellison, Shell Development, Houston, in developing a monograph on the analysis of corrosion problems with methods and concepts of chemical and electrochemical engineering.

To insure against isolation from other viewpoints, we have presented papers in four technical societies: ASTM, AIChE, NACE, and ECS. I chaired two symposia having international contributions:

Use of Chemical Engineering Methods in Controlling Corrosion
and Establishing Corrosion Mechanisms
AIChE and NACE (Joint Sponsorship), New York, 1977

Characterization of Current, Potential, and Mass Distributions
in Corrosion and Passivation Phenomena
The Electrochemical Society, Seattle, 1978

Publications (Calendar Year 1977): None

Theses (Calendar Year 1977): None

Theory of Polymers

Principal Investigator: Richard J. Gaylord, Ph.D.

Assistant Professor of Metallurgical Engineering

Supporting Agency: U. S. Department of Energy

Senior Staff: Richard J. Gaylord, Assistant Professor

Junior Staff: David J. Lohse, Research Assistant

Object: In bulk polymeric systems, the number of configurations which an amorphous chain can assume is limited. In a semi-crystalline polymer, amorphous chains are confined between crystalline regions. Block copolymers undergo microphase separation which results in the confinement of portions of chains between domains. A filled or reinforced elastomer contains non-polymeric material which is dispersed among the polymer chains. In cross-linked networks, the competition between segments of different chains for space and the entanglement of chains both result in the effective confinement of chains to limited regions within the network.

Two morphological features of the chain confinement in these systems affect their deformation properties: 1) the shape and spatial arrangement of the confining material; and 2) the types of amorphous chains between the confining material.

We are seeking to understand how these two features interrelate and contribute to deformation behavior. If this can be established, then it will provide a new way to develop polymeric materials with specific deformation characteristics for particular materials needs.

Results FY78:

Most Significant Accomplishments: Using the statistics of a polymeric chain confined by any number of rectilinear impenetrable walls which we previously developed, we have examined the role of tie chains (ends attached to opposite walls), cilia (one end attached to a wall), loops (both ends attached to the same wall), and floating chains (both ends unattached) in the deformation properties of several bulk polymeric systems. We have considered: semi-crystalline polymers with spherulitic and stacked lamellar structures; filled or reinforced elastomers; crosslinked networks; and block copolymers with spherical, cylindrical and lamellar domain structures. Our theoretical predictions of the stress-strain, modulus and swelling behavior of these systems are in very good qualitative agreement with experiment.

The most important aspect of this work is that it indicates that a previously neglected feature of polymer morphology, the amorphous material, can be used to create specific deformation properties in different polymeric systems.

Results Expected FY79: A deformation property which is common to semi-crystalline polymers, block copolymers and filled elastomers is that they

exhibit the so-called "Mullins effect". When these materials go through a load-unload-reload cycle, the stress during reloading is always lower than the stress during loading until the maximum strain level reached in the loading is regained. At that point, the stresses are the same. The stress-softening effect is important because most polymeric materials undergo a number of deformation cycles during their manufacture and also in their use.

We will be using our theoretical confined chain models of bulk polymers to examine this effect.

The other theoretical problem we will investigate is the birefringence of a polymeric chain confined by any number of rectilinear, impenetrable walls. When the basic formalism is established, it will be used to calculate the birefringence of confined tie chains, loops, cilia and floating chains.

Results Expected FY80: We will apply our results on the birefringence of confined polymeric chains to our theoretical models of semi-crystalline polymers, block copolymers, filled or reinforced elastomers and crosslinked networks. This, along with our previous results, will enable us to provide a complete description of the stress-optical properties of these bulk polymeric systems under various types of deformation.

We will also be extending our previous work on these systems and we will look at other polymeric deformation behavior such as the yield phenomena.

Relationship to Other Projects: Our theoretical work is related to the experimental work of several faculty at the University of Illinois: R. P. Wool has been studying the deformation and recovery behavior of semi-crystalline polymers; S. Wang is investigating the properties of polymeric composites; T. J. Rowland is examining semi-crystalline polymers and elastomers. We have a close interaction with these individuals.

We can also use our theoretical approach to examine polymeric chain motion. This is quite relevant to some of the work of J. Jonas and T. J. Rowland in the Materials Research Laboratory.

Finally, the polymers effort at the University of Illinois is continuing its expansion and additional faculty members working in this area are expected in the near future. There is now, and will continue to be, a very strong collaboration between the polymers people at the University of Illinois.

Publications (Calendar Year 1977):

R. J. Gaylord

Molecular Theories of the Deformation of Multiple Domain Polymeric Systems
Am. Chem. Soc. Polymer Preprints 19 (1) (1978)

D. J. Lohse and R. J. Gaylord

The Configurational Statistics of a Polymeric Chain Confined by Impenetrable
Barriers II: The Floating Chain
J. Chem. Phys. 66, 3843-3845 (1977).

Supported by National Science Foundation DMR 76-01058

R. J. Gaylord and D. J. Lohse

Block Copolymer Deformation
Polymer Engineering and Science (in press)

D. J. Lohse and R. J. Gaylord

The Amorphous Contribution to the Modulus of a Semi-Crystalline Polymer
Polymer Engineering and Science (in press)

R. J. Gaylord

Entanglement and Excluded Volume Effects in Rubber Elasticity
Polymer Engineering and Science (Submitted to)

Theses (Calendar Year 1977):

None

Dynamic Structure of Supercritical Dense Water and Aqueous Electrolyte Solutions

Principal Investigator: Jiri Jonas, Ph.D.
Professor of Physical and Analytical Chemistry

Supporting Agency: U. S. Department of Energy

Senior Staff: Jiri Jonas, Professor
John Schroeder, Research Associate

Junior Staff: Timothy H. DeFries, Research Assistant
Michael A. Fury, Research Assistant
Walter Lamb, Teaching Assistant
Gregory C. Munie, Research Assistant

Object: A study of the dynamic structure of various materials under extreme conditions of high pressure and high temperature represents the main theme of our research. Three main classes of materials are investigated: i) compressed supercritical water and aqueous solutions; ii) organic solids with a high degree of orientational disorder; and iii) polymeric materials. Our work currently focuses on investigating molecular motions, transport properties, and interactions at the molecular level in compressed supercritical water, heavy water and compressed supercritical aqueous electrolyte solutions. The order-disorder phase transformations are of main interest in our experiments on organic materials. The dynamic behavior of various polymeric systems under high compression is investigated in order to obtain a better understanding of structure-property relationship in polymeric materials.

The recently published Materials Sciences Overview (I, Executive Summary, ERDA 76/77/1) summarized reports of a series of workshops and recommended priorities in the future directions of energy related basic materials research. It is important to emphasize that all the various directions of the proposed research are identified as having high priority in the above document. In the following sections, references to this document are made.

The main techniques we currently use are the nuclear magnetic resonance relaxation experiments. NMR spectroscopy represents a powerful tool for investigation of motions and interactions at the molecular level. In order to extend the information content of some specific studies, we also use laser Raman spectroscopy to obtain the time dependence of various correlation functions. In the last several years, we continued to gain expertise in high pressure, high temperature NMR techniques, and as far as our current instrumentation is concerned, there is no other laboratory in the U.S.A. and/or abroad with comparable performance features of the NMR experimental system. In the area of NMR spectroscopy on materials at extreme conditions, we are the leading research group in the U.S.A. and abroad. Further development of new instrumentation for work at extreme conditions of high pressure and high temperature represents an important aspect of our studies.

The primary goal of our experiments on highly compressed supercritical water is the elucidation of the dynamic and static structure of this polar dense fluid which exhibits a number of remarkable properties such as: a) a complete miscibility with nonpolar fluids; b) the dissolved electrolytes dissociate into ions with very high mobility; c) the complex compounds of heavy metals can exist in it; and d) pure water itself shows very high electrical conductivity under such extreme conditions. There are many aspects of these experiments which have direct relevance to DOE's practical energy mission. Better knowledge of the properties of water and aqueous electrolytes at high temperature and high pressure will contribute to the solution of practical problems related to, e.g., geothermal energy utilization, coal gasification, etc. (pp. 3 and 21, Materials Sciences Overview I). In later stages of our research, in addition to aqueous solutions of electrolytes, we plan to investigate the dynamic behavior and transport properties of various ternary liquid systems such as H₂O-CO₂-hydrocarbon covering the range of temperatures and pressures used in tertiary oil recovery (pp. 9-20, Materials Sciences Overview, II. Workshop Reports, ERDA 77/76/2). There is one additional, important, practical aspect of our studies. Supercritical dense aqueous electrolytes are highly corrosive and, therefore, during our experiments, we shall gain valuable expertise about various materials in aggressive environment (p. 3, Materials Sciences Overview, I).

After we establish a firm experimental data basis on the dynamic behavior of aqueous electrolyte systems at extreme conditions of temperature and pressure, we shall devote our attention to a specific isotope enrichment process. There has been an isotope enrichment process proposed using high-pressure supercritical steam as a medium for dissolving ionizable inorganic salts and then using the steam solution in an electrolytic cell with counter-current flow. The efficiency of the isotope separation is considerably enhanced when superheated compressed steam is used as a solvent medium. Since the major problem in the separation of isotopes is the need for handling large quantities of feed materials with unneeded isotopes, even only a preenriching, relatively inexpensive process would be highly desirable. We plan to carry out a theoretical feasibility study for this isotope separation process and if proved encouraging, we shall build a laboratory setup to show the practicality of such an approach. In our planned experiments, we shall concentrate on ⁶Li and ⁷Li isotopes for the following reason. Lithium is used in the primary reactor cooling systems of pressurized water reactors. Highly enriched ⁷Li is desirable since it converts to nonradioactive helium upon neutron capture, whereas ⁶Li converts to tritium. If our experiments on lithium prove successful, then we may attempt a more difficult separation of the isotopes of uranium.

Our studies of the detailed nature of the order-disorder phase transformations and, in particular, the investigation of the kinetics of phase transformations in various organic solids, will contribute to our understanding of the phase transformations (p. 13, Materials Sciences Overview, I). Current exploratory experiments show promising direction of using an NMR technique to follow the kinetics of solid-solid phase transformation in organic materials.

Another class of materials under study are various amorphous polymers. Since many macroscopic properties of solid polymers are a direct result of molecular motions of polymer chains, experimental and theoretical efforts to elucidate the dynamics of motions in polymeric materials are of great basic and practical significance. For example, segmental chain motions underlie the phenomenon of elasticity and determine the glass transition. The number of NMR experiments performed on polymers under high pressure is so far very limited. Because many practical uses of polymers involve the presence of mechanical forces, this fact represents an additional important reason to use pressure as an experimental variable in studies of molecular dynamics in polymers (p. 18, Materials Sciences Overview, I).

Results FY78:

Most Significant Accomplishments: 1) Several studies by Franck (1968) have demonstrated the strikingly unusual properties of compressed supercritical water. Since NMR relaxation experiments yield valuable molecular level information about fluids, it is regrettable that, until now, no NMR studies of water under these extreme conditions have been performed. We have carried out the first NMR relaxation measurements on compressed water at supercritical temperatures (400-600°C) and densities from 0.05 to 0.35 g cm⁻³. The measurements were made using an argon-pressurized internally heated, titanium alloy NMR high pressure probe which can operate up to temperatures of 800°C and 2000 bar pressure. The experimental behavior of the proton spin-lattice relaxation times, T_1 , with density and temperature is characteristic for the spin-rotation interaction relaxation mechanism. Analysis of the data show that the spin-rotation interactions represent the dominant relaxation mechanism.

In our recent studies of non-polar fluids composed of spherical top molecules, we have successfully interpreted the behavior of the angular momentum correlation time, τ_J , in terms of the rough hard sphere model at high densities ($\rho > 2\rho_c$) whereas we proposed the modified hard sphere model for lower densities ($\rho > 2\rho_c$) to account for attractive forces. The theoretical interpretation of the data in terms of the modified rough hard sphere model indicates that water begins to resemble a hard sphere fluid at high temperatures and pressures. The efficiency of the angular momentum transfer during a collision is still affected by the strongly directional intermolecular forces between water molecules. The finding that compressed supercritical water begins to resemble a hard sphere liquid is important for several reasons. This result indicates that the short-ranged hard-core repulsive interactions begin to dominate over the strongly directional attractive forces between the water molecules; these directional forces are responsible for the tetrahedral hydrogen-bonded open structure of water at lower temperatures and pressures. Provided that our measurements of self-diffusion present the same picture, it would be then possible to propose a simple theoretical model to describe the transport properties of water under these extreme conditions.

2) Modern laser techniques allow the investigation of vibrational relaxation in liquids. It is possible to obtain separately the energy relaxation time and the dephasing time for a system, and these are times analogous to T_1

and T_2 in nuclear magnetic resonance. We have investigated the dephasing time since it is related to the spontaneous isotropic Raman line width.

Our experiments represent the first study of the separation of the effects of density and temperature on vibrational broadening. Only such experimental data allow one to test rigorously the current theoretical models. We have measured the Raman line shapes of the $\nu_1(A_1)$ C-H and C-D stretching fundamentals in liquid CHCl_3 , CDCl_3 , CH_3CN , and CD_3CN as a function of pressure and temperature. The vibrational relaxation rates are obtained from the isotropic component of the Raman band and our experimental results may be summarized as follows: (i) as the temperature increases, the vibrational relaxation rate increases; (ii) at constant temperature, the increase in density produces an increase in the relaxation rate; (iii) an increase in temperature at constant pressure results in an increased relaxation rate. The experimental vibrational data are interpreted in terms of the Kubo stochastic line shape theory and the collinear-isolated-binary-collision model of Fischer and Laubereau. The results based on the Kubo formalism indicate that dephasing is the dominant relaxation mechanism and that the interaction or modulation is very rapid. Interpretation in terms of the isolated binary collision model of Fischer and Laubereau leads to the following results: (i) pure dephasing is the dominant broadening mechanism for the isotropic Raman line shapes studied; (ii) the calculated dephasing rates as a function of pressure and temperature show good agreement with the measured relaxation rates.

3) As a part of our research on structure-property relationship in various polymeric systems, the frequency dependence of the proton spin-lattice relaxation times, T_1 , and the spin-spin lattice relaxation time, T_2 , have been measured as a function of temperature in several samples of cis-polybutadiene with different, well-characterized cross-link density. In contrast to T_1 experiments which are sensitive to motions in the MHz region, the NMR rotating frame relaxation time, $T_{1\rho}$, measurements probe slow motions in the kHz region. The general results of these experiments can be summarized as follows: i) cross-linking and decrease in temperature have a similar effect by freezing out the high frequency motions which tend to average dipolar interactions. As cross-linking increases, the liquid-like motions of one chain relative to another are essentially halted; ii) cross-linking also affects low frequency motions down to the kHz region ($T_{1\rho}$, measurements); iii) the $T_{1\rho}$ minima were found in the glass temperature region, T_g , and the shift of the minima is in the predicted direction for the Gibbs-DiMarzio theory of the T_g shift with increased cross-linking. At the present time, theoretical interpretation of the experimental data is under way, using two theoretical approaches which relate the microscopic relaxation of the nuclear magnetization to the motion of individual nuclear dipoles. We consider first, distribution of correlation times of molecular motions and secondly, use non-exponential correlation functions.

Other Results: 1) In our earlier studies on order-disorder transformations in various organic solids, we have found a marked hysteresis accompanying the order-disorder transition. All experimental results have indicated that NMR relaxation experiments are suitable to study the kinetics of these phase transformations. However, for purely practical reasons, we had to wait with our experiments on kinetics of the phase transformations until we developed a fully automated, computer controlled NMR spectrometer. The time scale of the experiments is such that manual measurement of the NMR relaxation times was not adequate. Our present NMR system is ideally suited for these experiments. The first system which we have studied is adamantane, $C_{10}H_{16}$, which is a saturated hydrocarbon whose molecules have a highly symmetrical cage-like structure. Adamantane undergoes a solid-solid phase transition at 208 K at 1 bar. In its high temperature, rotor, plastic α phase adamantane, has a fcc crystal structure whereas tetragonal β phase is the low temperature phase. The order-disorder transition retains the same center-of-mass topology--there is a tilt of 9° about the c axis. For further discussion, it is important to emphasize that there is a change in volume associated with this transition; the $\alpha \rightarrow \beta$ transition is accompanied with a volume decrease, whereas the opposite is true for the reverse $\beta \rightarrow \alpha$ transition. In our experiments, we bring the system into the region of thermodynamic stability of the other phase and follow the growth of this phase by the NMR relaxation measurements. We have found that the rate of phase transformation is approximately 10 times faster for the $\alpha \rightarrow \beta$ transition than for the reverse $\beta \rightarrow \alpha$ transition. The important factor determining the rate is whether one has a volume decrease or volume increase during the phase transition. During a transformation with volume increase, the formation of nuclei is resisted not only by the repulsion energy in the crystal but by the additional constraint that the volume expansion must take place against external confining pressure.

2) Much effort has been devoted in the past to the study of melting-freezing phenomenon and still no tractable theory exists to describe this transition correctly. In the past year, we have looked at some polar liquids such as nitrobenzene, acetonitrile and o-cresol in terms of their freezing behavior, employing light scattering techniques. We found for these liquids that they supercool readily far below their freezing points. Upon looking at these liquids from a Raman scattering viewpoint, where the different polarization components VV, VH and HH were examined, we found that the VH and HH line did not have their maximum intensities at the same vibrational frequencies as demanded by existing theory for normal liquids, but were shifted. This shift in the vibrational frequency was especially strong as the freezing point was approached and also VV and HH did not occur at the same vibrational frequency. Beside the unusual polarization effect observed in our studies, other experiments have observed certain anomalies in these liquids (i.e., viscosity anomaly, depolarized Rayleigh scattering, etc.). These results indicate the possibility of existence of some degree of ordering in polar liquids before the freezing point is reached.

Results Expected FY79: 1) As a continuation of our studies of the dynamic structure of supercritical compressed water, we propose to measure the self-diffusion coefficients of H_2O under these extreme conditions. Since Franck (1968) has reported the shear viscosities as a function of temperature and pressure in the supercritical region, our data will allow us to test the applicability of the hydrodynamic Stokes-Einstein equation at the molecular level. For a number of molecular liquids, we have found that this equation is valid in the slipping boundary limit. In contrast, we have found that this equation does not apply to water at low temperatures and pressures where the hydrogen bonded network is dominant. In view of our results for proton relaxation, which indicated that supercritical compressed water begins to resemble in properties a hard sphere liquid, it will be interesting to test whether at these extreme conditions the Stokes-Einstein equation describes the relationship between self-diffusion and shear viscosity.

Another set of experiments deals with the study of relaxation and transport properties of a series of aqueous electrolyte solutions such as H_2O -LiCl, H_2O - $CaCl_2$, etc., in the supercritical dense region. The question of the effect of various electrolytes on the dynamic structure of water, the nature of hydration of ions, the extent of ion pairing will be of main interest. We shall also attempt to measure the self-diffusion coefficients of the Li ions.

We propose to measure the density and temperature dependence of the proton exchange time in water by NMR. NMR represents a well-established tool in chemical exchange studies; both continuous wave high resolution techniques and pulse techniques were employed to determine the exchange rate. We plan to use water samples enriched to several percent in H_2O^{17} and carry out the measurement of the proton spin-lattice relaxation times in the rotating coordinate frame, $T_{1\rho}$, as a function of the magnitude of the spin-locking RF field, H_1 . From the dependence of the $T_{1\rho}$ times upon H_1 one can calculate τ_e , the mean lifetime of a proton between exchanges. The proton exchange reaction in water is of particular interest because of high mobilities of hydrogen and hydroxyl ions in water. The knowledge of the proton exchange time in water at supercritical conditions will help us to interpret theoretically the unusual properties of water under these extreme conditions.

We have designed a high pressure Raman cell that allows the attainment of $700^\circ C$ at a pressure of 6 Kbar. With this cell, we propose to carry out Raman line measurements of superheated water. Specifically, we wish to look at several O-H or O-D stretching vibrations in water (heavy water) at supercritical temperatures. Reduction of the density should lessen the effect of hydrogen bonding (which is reflected in the behavior of the O-H or O-D stretching vibrations) and consequently water should show behavior resembling that of normal fluids. The frequency range characteristic of intermolecular vibrations will be of most interest. This study should yield valuable information about the extent and nature of hydrogen bonding in supercritical dense water. Extension of these experiments to aqueous electrolyte solutions is straightforward.

In our earlier NMR studies of water and heavy water, we have reported anomalous behavior of many dynamic properties of water with initial compression at temperatures from -20 to $+40^{\circ}\text{C}$. Taking advantage of the phase diagram of water and heavy water, the pressure can be adjusted in such a way that H_2O and D_2O always remain in the liquid state even at temperatures below 0°C . Specifically, we propose to investigate the intramolecular bonding mode for water at about 1600 cm^{-1} , low frequency vibrational mode around 700 cm^{-1} , 400 cm^{-1} , and even closer to the excitation frequency. These experiments should provide additional information about the changes in the hydrogen bond network due to compression in this low temperature region where the open structure of water is dominant.

3) Our preliminary experiments on order-disorder transition in organic solids indicate that NMR relaxation techniques may develop into a very useful tool to study the dynamics of solid-solid phase transformations. We plan to continue work on these systems in the following main directions: i) to study effects of grain size on the rate of phase transformation; ii) to follow the effect of experimental conditions on the rate of phase transformation for the forward and reverse transition which in adamantane are accompanied of volume decrease and volume increase, respectively; iii) experiments on single crystals; iv) experiments on additional model systems which show different volume change accompanying the phase transitions; and v) both isobaric and isothermal experiments will be performed. If we succeed to obtain quantitative data for the rate of phase transitions, we shall attempt to interpret these in terms of current theoretical models. Detailed investigation of the hysteresis effects accompanying these phase transitions is also planned.

For many years it has been noted that polymeric systems show an unusual kink in the plots of various physical properties versus molecular weight. Properties such as viscosity and the frequency dependent loss and storage moduli all tend to exhibit this phenomenon. Such phenomena have been explained on the basis of molecular entanglements which are believed to form when polymer molecules are too long to move independent of one another without tangling.

Theoretical descriptions of such networks have been concerned with the effects of such entanglements on the motional spectra of polymers. Several authors have predicted a split in the motions of such systems into two categories: large scale, slow motions which are affected; and short range, high frequency motions which are insensitive to entanglement effects. While much work has been done using mechanical properties to investigate the entanglements concept, NMR studies of such effects have been very limited.

We propose to study the proton T_1 and $T_{1\rho}$ times in samples of polyethylene, polybutadiene and polyisoprene as a function of temperature, pressure and molecular weight. The reasons for such a study are as follows:

i) Using $T_{1\rho}$ and T_1 , the effects of molecular interactions over a broad spectrum of frequency can be ascertained. If entanglements are of a dynamic nature, effects on T_1 and $T_{1\rho}$ should be profoundly different.

ii) The selected model polymeric systems will allow us to investigate the effect of variable flexibility of the main chain on entanglements and also show whether the presence of methyl side-group substituent will affect entanglements.

iii) A first systematic study of the volume (pressure) effects on entanglement will be carried out. We hope to obtain experimental evidence on the possible dynamic nature of molecular entanglements.

4) As a continuation of spontaneous Raman scattering studies on prefreezing phenomena in polar liquids, we plan to carry out an infrared reflectivity study to demonstrate whether the Raman observations denote a TO (transverse optical) - LO (longitudinal optical) splitting effect. If the IR measurements do confirm the TO-LO splitting effect, what implication does this have in terms of freezing-melting phenomenon? The existence of TO-LO splitting implies a certain degree of ordering may exist in the liquid phase long before any freezing point is attained. This, of course, means that the assumption of a rapid change ongoing from the liquid to solid and vice-versa in terms of order-disorder is not a valid assumption. Our observations imply that the ordered structure of the solid does not abruptly cease to exist upon melting, but is carried into the liquid structure up to a sufficiently high temperature where kinetic effects then destroy the order giving the true disorder state of the normal liquid phase. The important questions to be answered by further work are: (i) What is the mechanism that allows this degree of order to be carried very far into the liquid state (i.e., clustering)? (ii) Non-polar liquids would have to be studied and compared to the polar liquid to see whether we are dealing with our purely Coulombic interactions in nature (i.e., long range interactions). (iii) What new stability criteria can be postulated that might improve the existing melting theories? (iv) The effect of density on the degree of ordering might give some very useful results. The observations of what we denote by TO-LO splitting in the liquid phase is really a precursor to freezing. A definitive experiment that has to be done on the polar liquids studied up to now is that of IR reflectivity. The IR reflectivity measurements allow the prediction of the position and shape of the Raman active LO modes. The infrared techniques will show whether TO-LO splitting exists and if it exists, it will confirm the existence of the degree of ordering (clustering) in polar liquids.

5) Recent computer simulation experiments have shown that molten alkali halides have an open structure containing many voids, quite different from a simple liquid such as argon. In contrast to simple liquids, where due to dominating repulsive forces, the packing geometry resembles that of hard spheres, the ionic melt structure is said to be "charge" ordered. Adams (1976) in his Monte Carlo calculations for molten KCl found that under

increasing pressure the structure of the liquid gradually changes from an open, charge ordered arrangement to one more nearly resembling that of a simple nonionic mixture. Lewis and Singer (1975) have reported molecular dynamics calculations for liquid sodium chloride and suggested that the temperature dependence of the self-diffusion constant is approximately linear but its density dependence is expected to be complicated.

In view of the above evidence for the open, charge ordered structure of molten salts, it would be of high interest to find out what is the effect of pressure on self-diffusion in several fused salts. We are quite optimistic about the feasibility of such experiments and propose to build a new high-temperature, high-pressure NMR probe suitable for work on molten salts. Depending on the results of this exploratory study, we may consider further systematic work in this direction using both NMR and Raman techniques. An additional system of interest is CaF_2 which is a superionic conductor at higher temperatures. The details of motion of the fluorine ions in CaF_2 will be investigated.

Results Expected FY80: The main theme of our research will be the dynamic behavior of various materials under extreme conditions of high pressure and high temperature. We expect to increase the upper temperature limit of our various experiments at high pressures so that we are able to investigate various additional systems such as fused salts.

In a continuation of our work on properties of water and aqueous solutions in the supercritical dense region we plan to extend our experiments to binary mixtures such as $\text{H}_2\text{O}-\text{CO}_2$ and ternary mixtures such as $\text{H}_2\text{O}-\text{CO}_2$ -hydrocarbon. If we find that additional experimental techniques will provide useful information about the systems studied, we may develop additional experimental techniques. The likely candidates are various electrochemical techniques on aqueous electrolytes and fused salts under conditions of high temperature and high pressure.

Depending on the results of the exploratory experiments on CaF_2 , we plan to follow the motional behavior of the F^- ions in superionic conductors such as PbF_2 and CaF_2 and to investigate, in particular, how compression affects the sublattice melting and whether compression changes the motional dynamics of the F^- ion. The effects of impurities on the motional freedom of the F^- ion will also be investigated.

After we obtain detailed experimental data on transport properties of various aqueous electrolyte systems at supercritical conditions, we shall resume work on the feasibility study for the proposed isotope separation process based on the countercurrent flow electrolytic process using high pressure supercritical water as a solvent medium for ionizable salts. In the case that our theoretical feasibility study for the isotope separation proves promising, we intend to build a small scale laboratory setup to attempt the separation of the ^7Li and ^6Li isotopes.

During our experiments at high pressure and high temperature, we have often observed large effects of stress-induced corrosion. We consider carrying out several exploratory experiments and attempt to characterize the corroded surfaces using the various techniques such as ion microprobe, Auger spectrometer, etc., available in the Central Facilities of the Materials Research Laboratory. Depending on the results of these exploratory experiments, we may consider starting experiments on corrosion of materials in aggressive environments under conditions of high temperature and high pressure.

The relative emphasis on the research dealing with order-disorder phase transitions in organic solids and the work dealing with the dynamic behavior of various polymeric materials will naturally depend on the results of previous years. Of considerable interest is the study of the dynamic properties of various high temperature polymers (e.g., polyimides) as a function of temperature and pressure. In view of our current experiments on prefreezing phenomena, we may start systematic experiments dealing with the solid-liquid phase transformation. Development of new instrumentation for work at extreme conditions will continue to be an important aspect of our research effort in order to continue and improve our expertise in this specific field.

Relationship to Other Projects: Since our high pressure, high temperature NMR experiments are unique, there is no duplication of our effort with laboratories elsewhere in the U.S.A. and abroad. However, close contact is maintained with NMR and high pressure research in other laboratories.

In view of the fact that our work on supercritical compressed water and aqueous electrolytes is of high relevance for research on problems related with non-nuclear energy sources such as geothermal energy sources and underground energy generation, we anticipate that our studies will help laboratories dealing with these important projects. Our expertise in behavior and properties materials at extreme conditions of high pressure and high temperature may lead to a closer collaboration with some of these laboratories.

We plan to provide our data on superheated compressed steam and compressed supercritical aqueous electrolyte solutions to the Isotope Development Center at the Oak Ridge National Laboratory. If our small scale laboratory experiments dealing with separation of isotopes prove successful, we intend to develop a close working relationship with the Isotope Development Center at the Oak Ridge National Laboratory. If evaluation of the process at a practical scale is decided upon, we plan to assist with our expertise gained during our experiments.

We are presently collaborating with T. J. Rowland (Metallurgy and Mining) in an NMR study of the effect of cross-linking on molecular motions in cis-polybutadiene. As the experimental polymer studies progress to include entanglement and topological considerations, the theoretical expertise of R. Gaylord (Metallurgy) will be most helpful. The current and proposed studies of polymers do not represent an isolated effort at the University of Illinois because there are a number of researchers in the area of polymer engineering.

Our exploratory NMR experiments on the kinetics of order-disorder phase transformations in organic solids appear very promising and we expect that a close collaboration with theorists at the University of Illinois, or off campus, may prove fruitful. Planned development of NMR instrumentation for high pressure work at temperatures up to 1300°C may lead to experiments dealing with fast ion transport in materials such as CaF_2 . This work will result in close collaboration with the active group of researchers in the Department of Physics who investigate superionic conductors. The success of our laser Raman scattering experiments can be related to our interaction with M. V. Klein (Physics), who is an expert in optical spectroscopy. Daily research discussions with H. G. Drickamer (Chemistry, Chemical Engineering, and Physics) prove extremely valuable.

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Also supported by U.S. Air Force AFOSR-77-3185 and the National
Science Foundation Grant MPS-19428

AK-01-02-01-2 Mechanical PropertiesHydrogen Behavior in BCC Metals

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Object: Our program is directed toward understanding the behavior of light interstitial elements in solids and the effects of these interstitials on the properties of solids. We are focusing our efforts on hydrogen and its isotopes in the Group Vb bcc metals, Nb, V, and Ta and in the fcc metals Ni and Pd. This area of research provides a happy confluence of basic and applied research problems. The behavior of light interstitials is largely governed by quantum effects and, hence, is of great theoretical interest. At the same time, the effect of hydrogen on the properties of solids, the mobility of hydrogen, and the properties of the hydrides are all of interest in engineering materials problems such as hydrogen embrittlement, stress corrosion, energy storage in hydrides, energy transport, and in the properties of amorphous semiconductor solar cells.

Many energy related systems operate under conditions of high hydrogen fugacity and are subject to materials failure due to hydrogen entry into the solid. This can occur from solute hydrogen or gaseous hydrogen, in which case the failures are generically termed "hydrogen embrittlement" or "hydrogen attack"; or from a corrosive environment in which instance the failures are classified as "stress corrosion". In all cases, the critical parameters of the failure involve a) hydrogen transport across the interface between the solid and its environment, b) hydrogen diffusion or transport to regions of high stress concentration, and c) decrease of the local fracture strength which accompanies the increased hydrogen concentration and/or the formation of a hydride.

There are many examples of existing and proposed energy systems for which control of the above type of failure is crucial. Nuclear and non-nuclear electrical power systems for which stress corrosion of stainless steel is a continuing problem, pipelines and well casings for which "sour gas" fracture is a problem, coal gasification systems which are subject to a variety of hydrogen related failure problems at both low and high temperatures, fusion reactors for which fracture and tritium containment must be considered to be major problems can be cited among many others. The extent to which our materials usage will be limited by hydrogen related failures

can be expected to increase as we design energy systems which must operate in increasingly aggressive environments.

Our program is designed to develop fundamental understanding of the constituent processes involved in hydrogen related failures. As discussed below, we are studying hydrogen mobility in bcc metals with a particular emphasis on understanding the phonon assisted tunneling process and the interaction of hydrogen with trapping sites. We are examining the detailed mechanisms by which hydrogen enters the solid from the gaseous phase and the effect of specific adsorbed molecular species on this process. We are also studying the effects of hydrogen on the phonon behavior of hydrides and high hydrogen concentration alloys to attempt to determine why these fail in a brittle fashion.

As will be discussed below, we are interested in beginning to study some of the detailed crack tip processes using x-ray topographic techniques. This effort, which is directly related to hydrogen embrittlement, is feasible due to the availability of high intensity x-ray sources such as rotating anode tubes and synchrotron sources. We will begin this effort if additional funding is available.

Energy storage technology is another area with which our research is closely interfaced. Some of the major technological problems involve the use of hydrides as storage media. To successfully utilize such a system requires an understanding of the properties of the hydrides as well as the mechanism of hydrogen transfer into and out of the solid. Another aspect of the problem involves the detailed behavior of hydrogen at the solid surface. This is of importance in some of the proposed systems for hydrogen generation by direct thermal or catalytic processes.

Acoustic relaxation methods are being applied to studies of hydrogen mobility in the bcc metals. A continuation of the Gorsky effect studies of hydrogen diffusion in niobium is being directed toward extending the accessible temperature range. Since our previous work has shown the low temperature behavior to be highly non-classical in nature, we are attempting to make measurements at temperatures below 100 K. We will be studying the relationship between the quantum tunneling which characterizes the local jump process and the long range migration. At the high temperature end of the measurements, we are primarily concerned with the effects of trapping on the hydrogen mobility.

In previous years, we have completely characterized the nature of the O-H trapped hydrogen defect in niobium. We will now be studying certain aspects of the N-H defect, particularly to determine how the hydrogen behavior depends on the nature of the trap. In a continuing attempt to study the behavior of hydrogen at very low temperatures, we will continue to develop the anelastic piezoresistance technique. This rather novel method should enable us to study the behavior of hydrogen in very dilute solutions and therefore at very low temperatures.

A new research direction is being developed as an outgrowth of our Raman studies. We are applying a combination of Raman, Auger and permeation techniques to examine the detailed mechanisms of hydrogen entry into niobium

and nickel crystals. In addition, we will be investigating the role of specific adsorbed molecules such as H_2S , H_2O and SO_2 on this process. Raman spectroscopy will be used to characterize the vibrational modes of the adsorbed species in the presence of and absence of hydrogen. Auger spectroscopy will be used to characterize the surface chemistry and permeation methods will be used to measure the rate of hydrogen entry from the gas phase under characterized surface conditions.

If funding is available, it is proposed that we begin to apply diffraction techniques to a study of crack tip processes. We would examine the stress state and the plastic zone at a crack tip and how these are affected by the flux of hydrogen to the crack. This work would make use of the high intensity x-ray source in the MRL as well as the synchrotron x-ray source at Brookhaven Laboratory as it becomes available. The studies require high intensity sources, particularly as we would like to examine the behavior of slowly propagating cracks.

In addition to the above studies, a number of our joint research programs will be continued. The μ^+ diffusion and trapping studies, which are jointly being carried out with various laboratories, will be continued in niobium and will be extended to tungsten crystals in which niobium will be used as a trapping site. These studies allow us to further understand the non-classical isotope dependence of hydrogen mobility. Our neutron scattering studies of phonon modes associated with hydrogen in niobium will be continued as these are leading to an understanding of the effects of hydrogen clustering and fluctuations on the bonding of the solid. These measurements are being carried out on the hydrides as well as on the solid solutions and are being correlated with elastic constant measurements on these alloys. A cooperative effort with Professor Granato is being undertaken to use elastic constant methods to study hydrogen tunneling at temperatures below 4 K. It is expected that these will lead to further understanding of the delocalized nature of the hydrogen interstitial which was first observed using specific heat and thermal conductivity measurements.

Results FY78:

Most Significant Accomplishments: (1) The phonon dispersion curves and the diffuse inelastic scattering around primary and superlattice reflections were measured using neutron scattering methods for high concentration NbD and NbH alloys. These measurements were carried out in the solid solution α' phase as well as in the β hydride phase. A variety of new phenomena have been uncovered which bear on the α' - β phase transition, on the mobility of H(D) in the α' and β phases and on the reasons why the α' and β phases are extremely brittle.

One of the most significant results is the observation of a 19 MeV phonon mode in $\text{NbH}_{0.82}$ and $\text{NbD}_{0.82}$ which does not exhibit any dispersion throughout the Brillouin zone. In addition to this particular mode, the data suggests the possibility of other similarly non-dispersive modes at higher and lower energies. These phonon energies are the same for H and D, and for the α' and β phases, although the phonon lifetimes depend on the isotopes

and on the phases. The non-dispersive phonons are not the optic modes which lie at much higher energies. While a detailed understanding of these modes is not available, it does appear that they result either from the quantum tunneling of H or D between sites of different energy or from heterophase fluctuations which occur close to the α' - β phase transition.

The occurrence of this 19 MeV phonon mode appears to be accompanied by a marked softening of the 110 LA phonon at the Brillouin zone boundary. This softening, which has not been previously observed, results from an interaction between the 19 MeV phonon and the 110 LA mode. Since the {110} plane is observed to be the cleavage plane in the α' and β phases, softening of the phonons may be related to the brittleness of these phases. Theories of cleavage suggest that a decrease in the 110 LA phonon energy at the Brillouin zone boundary should result in a decrease in the energy required for cleavage on the {110} plane. Thus, these neutron scattering observations may give some insight into the problems of hydrogen embrittlement.

The neutron scattering results are also of interest in connection with our previous results on the α' - β phase transition and the softening of the elastic constants which accompany it. These results were interpreted as indicating the presence of heterophase fluctuations of the β hydride phase within the α' phase region. To some extent the diffuse neutron scattering observed in the α' phase has supported this conclusion. Our theoretical interpretation of these diffuse scattering measurements suggests that β phase fluctuations can occur over the entire temperature range where elastic softening is observed in the α' phase.

The detailed understanding of the elastic and phonon properties of the NbH(D) solid solutions and hydrides and of the fluctuation phenomena which accompany the phase transition are of interest in developing an understanding of the mechanisms of hydrogen embrittlement. One of the critical questions in this subject is why the formation of a hydride or the stress induced concentration of hydrogen in solid solution results in a marked decrease in the stress to fracture the solid. While we cannot yet answer this question, we expect to be able to develop an understanding of it based on our measurements.

(2) We have continued to explore aspects of the quantum behavior of light interstitials in solids. Significant results have been obtained in the past year which cannot yet be incorporated into the existing theories of diffusion. Primary among these is the strong isotope dependence which was observed for H, D and T in Nb and now for μ^+ in Nb. In the case of the first three isotopes, the theory suggests that the diffusion activation enthalpy should be isotope independent while experiment shows a strong dependence. In the case of the μ^+ results, the isotopic mass range has been extended down to 1/6 that of the proton. In this case, we believe we have been able to directly observe the transition between the quantum tunneling behavior, which is characteristic of the low temperature behavior and which was postulated by us on the basis of heat capacity measurements of the Nb-H(D) system, and the "hopping" behavior expected at higher temperatures. These results may provide strong support for the basic quantum tunneling model of light interstitial mobility in solids.

Other Results: The studies of the low temperature behavior of He in Nb have shown a) trapping of He at O interstitials, and b) the formation of He bubbles at grain boundaries at temperatures near room temperature. This result may be highly significant in view of the severe intergranular embrittlement caused by helium.

Expected Results FY79: The general understanding of the mobility of light interstitials in bcc metals, which is based on our work as well as that of others, is:

- a) Delocalized hydrogen at very low temperatures $T \leq 4$ K. The hydrogen moves in a ring on the {100} planes. Long range diffusion involves hopping from ring to ring by the Flynn-Stoneham mechanism.
- b) Localization of the hydrogen in particular tetrahedral sites as the temperature is increased. Quantum tunneling occurs between sites on a particular ring. Motion between rings is by the Flynn-Stoneham mechanism.
- c) Trapping occurs at interstitial solutes, dislocations, etc.
- d) At elevated temperatures $T > 100$ K, the long range diffusion can be described by an Arrhenius temperature dependence although the detailed behavior remains quantum tunneling within a ring and phonon assisted tunneling between rings.

In FY79 we expect to obtain further results to elucidate this model of hydrogen diffusion. It is expected that the Gorsky effect measurements of H diffusion in niobium will be completed and that the effects of trapping will be established. Of particular interest will be the question of whether H diffusion in the temperature range above 100 K can be described as an Arrhenius relation or whether quantum effects are present even at these temperatures. While our previous results on the isotope dependence of H diffusion have clearly shown that quantum effects are important in this temperature range, it has not been established how these affect the temperature dependence of the diffusivity.

In this period, the characterization of the N-H defect should also be completed. We will then be in a position to relate the behavior of hydrogen in trapped sites, such as at O and N interstitials, to the long range diffusion measured by the Gorsky effect. A result of particular importance will be the dependence of the phonon assisted tunneling behavior on the nature of the trapping site. This will be available on comparison of the N-H results with our previously obtained O-H results.

We will continue to develop the anelastic piezoresistance technique to enable us to study the behavior of dilute hydrogen alloys at low temperatures. This method, although beset with experimental difficulties, holds great promise for establishing the nature of the hydrogen diffusion process at temperatures below 100 K. Since the hydrogen solubility at these low temperatures is extremely small, the standard anelastic methods are not useful. We hope to overcome these limitations with this new method.

The use of Raman and Auger spectroscopic techniques with permeation methods to study the mechanisms of hydrogen entry into Nb and Ni will be continued. These two metals were chosen to typify metal-hydrogen systems which have a coherent, relatively impermeable oxide surface film and a non-protective oxide respectively. Both systems have well-characterized hydrogen diffusivities. Particular attention will be paid to the effects of adsorbed molecular species on the transfer of hydrogen across the solid-gas interface. The Raman technique will be used to determine the change in the vibrational modes of molecules such as H_2S when they are adsorbed on a clean metal surface and then when the adsorbed molecule is exposed to hydrogen. The rate of entry of hydrogen will be measured using permeation techniques. Since H_2S is known to accelerate hydrogen entry and SO_2 and H_2O are known to retard it, we will focus our attention on these systems. We also hope to be able to alter the surface orientation, grain structure, and the dislocation density at the surface in order to examine the effect of these variables.

We will continue to expand our efforts in the area of neutron scattering as applied to the high H concentration alloys of Nb and Ta. The structure of these alloys and the phonon dispersion relations are of great interest in understanding the mechanical properties of the hydrides and the high concentration solid solutions. The effort will be collaborative with the Argonne group and the Brookhaven group. We will continue to look at the local mode behavior of H in the hydride single crystals and to correlate these results with the Raman studies where this is possible. It is expected that these studies will help us understand the hydrogen diffusion mechanisms as well as the nature of the various phase transitions in the hydrides. Consideration of the relationships between the phonon properties and the fracture behavior will be started in an attempt to understand why high hydrogen concentration alloys and hydrides are so extremely brittle.

We expect to continue our collaborative efforts to study μ^+ diffusion in the bcc metals. We expect to concentrate on the interaction of μ^+ with impurities having a magnetic moment, such as Nb in W, in order to study the detailed trapping and diffusion mechanism.

We are proposing a new effort in the application of x-ray methods to study fracture and crack tip processes during hydrogen embrittlement. This effort will be started only if increased funding is available. In this program, we will be examining the stress field and plastic deformation at static and at slowly propagating cracks using x-ray topographic techniques. The questions we shall be addressing are: a) Can x-ray techniques be developed to enable a detailed mapping of the elastic stresses to be carried out? b) Can the plastic zone at a crack tip be studied? c) How are the elastic stresses and the plastic zone affected by the flux of hydrogen to the crack tip? d) Can the x-ray method be used to study stress induced hydride formation at the crack tip? These studies will require the use of a high intensity x-ray source such as a rotating anode tube or a synchrotron source. It is expected that a rotating anode tube will be available in the MRL and that use will be made of the Brookhaven synchrotron when it becomes available. These experiments, which are feasible only because of the high intensity sources, will also require image detection and enhancement facilities.

If successful, they should lead to a very significant increment in our understanding of hydrogen embrittlement and the fracture behavior of solids.

Expected Results FY80: We expect to continue our studies of the light interstitial diffusion mechanisms with an emphasis on the behavior at very low temperatures using anelastic piezoresistance and neutron scattering. In the former case we will be studying very dilute alloys; in the latter case we will be using high concentration hydrides. We will be emphasizing studies of the transition between the delocalized tunneling behavior which occurs at higher temperatures.

We hope to extend our neutron scattering efforts to other hydrides and particularly to higher concentration hydrides such as NbH_2 . We will emphasize both the phonon behavior and studies of the phase transitions between hydrides.

The studies of hydrogen transfer across solid interfaces will be continued. Emphasis will be placed on determining the nature of any particularly active surface sites for hydrogen entry and the effects of adsorbed species on these sites. It may be possible to characterize these sites and the adsorbed species by the use of STEM and energy analysis of the diffracted electrons.

The x-ray studies of crack tip processes will be continued. During this period, the techniques will have been developed and the limitations of the experiment understood. Dynamic studies of slowly propagating cracks will be started using Nb-H and Ni-H alloys as model systems.

Relationship to Other Projects: The capabilities developed in our laboratory for the study of light interstitial diffusion are rather unique. As a result, we have maintained close relationships with a number of other research groups both in this country and in Europe. In some cases, we are providing samples, which can only be produced by our facility, for study, and in other cases we are carrying out joint research programs.

At the University of Illinois, we have a joint program with Professor M. V. Klein on the use of Raman spectroscopy to study H in metals and the adsorption of molecules such as H_2S on surfaces. A very valuable interaction with Professor C. P. Flynn directed toward the theory of hydrogen behavior is being continued. We are working with Dr. A. V. Granato's group on a study of H in Nb using very low temperature elastic constant measurements.

The neutron scattering experiments are being carried out jointly with Dr. T. Brun and M. Mueller of Argonne National Laboratory and with Dr. S. Shapiro of Brookhaven National Laboratory.

The μ^+ studies are being carried out jointly with Dr. A. Fiory of Bell Telephone Laboratory, Dr. K. Lynn of Brookhaven National Laboratory, a group of scientists at Los Alamos and Sandia Laboratories, and W. J. Kossler of the College of William and Mary.

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C. G. Chen and H. K. Birnbaum
Resistivity Studies of Interstitial Helium Mobility in Niobium
J. Nucl. Materials (accepted for publication)

Theses (Calendar Year 1977):

None

Characterization of Compounds and Alloys

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Mark E. Twigg, Research Assistant
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Object: The goal of this research is the fine scale characterization of materials important in energy conversion systems. Characterization includes microstructure, crystal structure, microchemistry, distribution of phases and orientation relationships of phases. Instruments and methods which allow such characterization on a fine scale are still in their infancy, so that the technique development, especially of analytical electron microscopy, forms a large part of this proposal. We will examine these techniques to materials and phenomena important in solar, fossil and nuclear energy conversion systems. In particular, we will examine the stability of compounds under various conditions of temperature and atmosphere and will relate the microstructure and chemical composition to physical properties of the materials.

Complete characterization of a material on a fine scale (in the angstrom region) is extremely difficult. However, techniques are being developed which permit this to be done in situ in an electron microscope at the ultimate resolution of the instrument. These techniques, grouped together under the term analytical electron microscopy (AEM), have become subjects of considerable interest because many properties of multiphase materials are controlled by structural and chemical variations in the range of a few to a hundred or so angstroms. We have contributed significantly in the development of these techniques during the past few years.

The basic instrument of AEM is a scanning transmission electron microscope (STEM) whose electron optical system allows image and area selection to be made down to extremely small incident electron probe diameters ($\geq 2 \text{ \AA}$). The result is that, in principle, spatial observations can be made down to $\sim 3 \text{ \AA}$ (point) or $1.4 \text{ \AA}$ (lattice). The geometry of the electron beam and the intrinsic characteristics of radiation detectors do not permit chemical characterization of compounds to be made at this level, still use of an

energy dispersive x-ray analyzer makes microchemical determinations possible for elements with $Z \geq 11$ on a scale of about 200 Å. Part of this limitation is a result of specimen contamination in the vacuum system of the JEOL which we use.

Crystallographic determinations are also possible on a fine scale. Selected area diffraction should be possible, in principle, from volumes excited by an incident probe of < 30 Å. However, instrumental factors have again not permitted this resolution to be achieved. Using our JEOL-200, we have been able to define operating conditions which allow selected area diffraction patterns to be obtained from areas of about 200 Å using the stationary diffraction convergent beam method. The electron probe size was limited by a combination of beam convergence (caused by an insufficiently bright gun) and specimen contamination.

Clearly, electron gun brightness and specimen contamination provide significant limitations of resolution both in use of diffraction capabilities and elemental analysis of conventional microscopes. Furthermore, the important light elements are out of range of usefulness of the silicon (Li) detector used for characteristic x-ray detection. These limitations have been circumvented by our acquisition of a new scanning transmission electron microscope (VG HB5) which is equipped with a UHV vacuum system and a field emission gun. Furthermore, an electron energy loss spectrometer has been obtained so that, in principle, light element analysis can be performed through studies of the absorption edges. A large part of the program is dedicated to development of techniques to allow reliable qualitative and quantitative techniques of analysis for the light elements.

Electron energy loss spectroscopy shows great promise in a number of areas of metallurgy and physics. Our primary interest is in the quantitative analysis of light elements by study of the absorption edges present in the loss spectrum. There have been some examples of qualitative and quantitative analysis using this technique, but the subject is still new and much development is needed. One interesting light element, hydrogen, cannot be analyzed in this way since its interaction with the electron beam does not produce an absorption edge. However, hydrogen present in a metal does alter the local electron density and therefore changes the shape and position of the plasmon loss peaks. Experiments are planned to determine whether studies of plasmon losses will lead to qualitative and/or quantitative analysis of hydrogen in metal foils.

A number of materials relating to energy conversion systems are candidates for study. For example, thermal absorbers are frequently oxides of refractory metals such as molybdenum, chromium or nickel. Although the gross chemical composition is known, studies of the detailed stoichiometry of these compounds, their stability during the temperature changes and their stability in the presence of corrosive or erosive atmosphere are needed. The various metal "blacks" formed by electrolytic deposition are important candidate materials. Also important is the analysis of compounds formed on insulators which might be used in reactors forming parts of energy conversion systems.

Using ion beam thinning, it should be possible to examine the structure of protective or catastrophic layers formed on the surface of ceramic liners as reactions proceed.

The chemical characterization of coal, especially measurement of its impurities, will be undertaken. Coals vary greatly, it is known, in composition and nature of trace impurities. Although the presence and overall concentration of these impurities has been studied for a long time, the application of microtechniques of analysis is only beginning. STEM offers the possibility of studying the segregation of impurities and of characterization of the structure and composition of microphases on a scale not previously achieved. The following appear to be possible: the characterization of mineral matter in coal; the nature of the distribution of sulfur, both within organic material and concentrated as sulfides; the presence and nature of silica and carbonate minerals; the characterization of chars which result from partial decomposition of coal. One difficulty of these analyses will be the elimination of volatile products from coal before it is inserted into the microscope. Since the specimen chamber must operate in an ultrahigh vacuum, specimens containing volatile constituents which outgas during examination cannot be used. However, degassing of the specimens of volatile constituents before they are inserted in the microscope appears to be feasible.

An additional area of investigation is examination of steps in the reduction of ores to the constituent metals (or characteristic simple compounds). We have completed an investigation of the many steps and substeps which occur in the reduction of tungsten oxide to alpha tungsten. During that study, we were forced to use conventional x-ray analysis for determination of particular oxides present at various stages of reduction. Thousands of x-ray analyses were required; these were carried out by the Westinghouse Lamp Division. Also, analyses for oxygen, which would have been possible with AEM facilities, could not be performed.

Results FY78:

Most Significant Accomplishments: The most significant accomplishment has occurred in our study of carbide precipitation in V-5Ti-C alloys. The aim of the study has been to determine the effects of Ti additions to the precipitation of carbides in V-alloys. At low temperatures (below 800°C) Ti atoms are relatively immobile, so the carbides formed are nearly the binary V-C carbides we observed many years ago. At high temperatures where Ti may diffuse at appreciable rates, the carbide precipitation process is markedly altered. The crystal structure changes from the hexagonal V₂C-type to a cubic MC-type phase possessing the sodium chloride crystal structure. The main question then was to determine the equilibrium concentration of Ti in the carbide. This has been done using AEM, and the carbides were found to be V₂TiC₃. These compounds are remarkably stable in size and should provide excellent high temperature strengthening.

Other Results: A major task of this year was the accumulation of funds (80% from non-contract University sources) for purchase of the most modern scanning transmission electron microscope with capability of energy loss spectrometry. That instrument has been installed and is operating. Only two such instruments are available in the nation, one at MIT and the other in our Laboratory. The JEOL-200, which has some of the capabilities of the present instrument, remains in operation. It does not have the energy analysis capability, but will continue to be useful for heavy metal analysis. We have nearly completed the development and installation of computer capabilities and memory storage for direct interfacing with both of these machines. It may also be able to interface our microscopes with the DEC central computer.

Results Expected FY79: The conditions for reliable operation of the various analytical techniques and the limits of their capabilities for materials characterization will be determined. The diffraction capabilities and x-ray analysis features will be optimized. Necessary standards for the x-ray work will be established.

A major undertaking will be the development of energy loss spectroscopy for the microchemical analysis of light elements. Specifically, two types of experiment will be performed. First, we shall make energy loss measurements on oxides (probably of molybdenum) and using these results determine methods that lead to successful quantitation of results. Secondly, experiments will be performed on metal-hydrogen alloys to determine whether changes in shape and position of the plasmon losses can be used to make location and analysis of hydrogen possible. Finally, an energy loss spectrometer will be designed and constructed that will possess an energy resolution of less than 0.5 eV and permit fine structure of absorption edges to be measured.

Results Expected FY80: Part of this work is designed to develop the capability of characterizing small volumes of solid (or thin layers) completely, as far as their crystal structure and chemistry is concerned. This itself is an important undertaking. However, once this capability is demonstrated, one will make and relate physical property measurements to the microcrystallography, the defect structures, or the microchemistry of materials important for solar, coal-related and other energy conversion systems. We are fortunate in the area of coal research to have access to an extensive catalog of identified coal samples collected over many years by the staff of the Illinois State Geological Survey; measurements we make on these samples will be made on a collaborative basis with that staff.

Relationship to Other Projects: A large number of interactions have been developed with MRL, University of Illinois and off-campus investigators, and in each case the interaction has been mutually advantageous.

In the MRL, interactions exist with E. N. Pugh (Metallurgy) involving the examination of fracture faces in the STEM by "back-thinning". Cooperative work exists with C. M. Wayman (Metallurgy) concerning phase transformations in

beta brass. Finally, work on small crystallites of Si on SiO₂ substrates has been performed with C. A. Evans (Chemistry).

Within the campus but outside of the MRL, our AEM studies have led to joint programs with R. Mehrabian (Metallurgy) involving powder metallurgy and laser skin melting.

Outside the campus, our work on AEM has led to two loose interactions with Professor J. Silcox (Cornell University-Physics) and Drs. Maher and Joy at Bell Laboratories.

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Supported by National Science Foundation DMR-76-01058 and CHE-76-03694

M.S. Theses (Calendar Year 1977):

D. V. Beggs (C. A. Wert, Adviser)

Carbide Formation at High Temperature in Vanadium-Titanium-Carbon Alloys

S. M. Bruemmer (C. A. Wert, Adviser)

High Temperature Precipitation in Vanadium-Titanium-Carbon Alloys

Ph.D. Theses (Calendar Year 1977):

None

Mechanism of Stress-Corrosion Cracking: Propagation Studies

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Supporting Agency: U. S. Department of Energy

Senior Staff: E. Neville Pugh, Professor
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Junior Staff: Dennis V. Beggs, Research Assistant
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Object: This research is part of a broad study at the Urbana-Champaign campus on the mechanisms of stress-corrosion cracking (SCC) and hydrogen embrittlement (HE) of engineering materials. These failures occur widely in the present generation of nuclear reactors, e.g., austenitic stainless steels in high-purity water systems, nickel-base alloys in steam generators, Admiralty Metal in condensers, and zirconium and magnesium alloys used for fuel cladding; and it is expected that such failures will pose a serious problem in future types of reactors and in other developing energy industries, particularly in coal gasification and in the harnessing of geothermal energy.

In view of the enormous costs of stress-corrosion and HE failures and the frequency with which they occur, it might seem surprising that industry has not learned to avoid them. The continuing incidence of such failures is due in large part to the fact that the underlying mechanisms are poorly understood; this, in turn, stems from the complex nature of the embrittlement phenomena, which involve the interaction of metallurgical, chemical and electrochemical factors. The problem is complicated by uncertainty concerning the number of mechanisms which operate--it is becoming clear that the term SCC does not represent a single process but the number of basically different mechanisms which occur in practice remains to be established. It is probable that more than one type of failure can occur in a single material-environment system, and that the different processes are competitive, so that measures to prevent one may not influence or may even accelerate another.

Our previous studies lead us to the view that practical cases of SCC can be grouped into two basically different types, one in which propagation occurs by anodic dissolution (generally intergranular) and another in which propagation is mechanical (generally transgranular). At the present time, the consensus among workers in the field is that the dissolution type occurs by the film-rupture model, that is, by the preferential anodic dissolution of film-free metal at the crack tip, exposed by localized plastic deformation, while the non-deforming crack walls remain protected by a passive film. The details of this process require considerable further attention. For example, the rate at which exposed metal becomes repassivated

is known to play a controlling role in SCC, yet the specific effect of alloying elements on the repassivation process is poorly understood. Further, repassivation is thought to be slower at grain boundaries, accounting for the intergranular path of failure, but the reasons for this are not established.

The mechanical type of SCC is poorly understood. Our previous work indicates that these failures generally occur by cleavage, that is, by brittle mechanical failure, and that crack propagation is discontinuous. The cause of embrittlement has not been established but there is considerable interest, and controversy, in the possibility that it is due to hydrogen absorption--that is, that T-SCC is a form of HE. It is well established that HE occurs in certain materials, e.g., high-strength steels and the refractory metals such as vanadium and niobium, and that it can result from internal hydrogen, introduced by cathodic or high-temperature gas charging, or during exposure to external gaseous hydrogen. Two mechanisms of HE are currently being advocated, the first postulating that hydrogen reduces the bond strength of the host material (decohesion model), and the second proposing that cracking proceeds by the formation and fracture of brittle, stress-induced hydrides. It is possible that each of these mechanisms may operate in particular cases or, alternatively, that only a single mechanism is responsible for all cases of HE. An alternative model for the mechanical type of SCC involves selective dissolution of a certain component from an alloy, but this approach is currently attracting little attention.

Our DOE program to date has focussed on the mechanism of the mechanical type of SCC and has involved the transgranular, cleavage-like form of failure, mainly utilizing fractographic and acoustic-emission techniques. This work is continuing, and is being directed towards the use of the transmission electron microscope (TEM) and other electron-optical methods in an attempt to identify the embrittling phase or species. In addition, we are beginning some work on passivation, related to the dissolution type of SCC. It is hoped that this work will lead to interaction with R. C. Alkire, part of whose current DOE-supported work involves the breakdown of passive films and the resulting localized corrosion.

Results FY78:

Most Significant Accomplishments: The most significant results involved studies of Admiralty Metal in aqueous ammonia solutions, and relate to the general question of the mechanism of T-SCC. The transgranular fracture surfaces are cleavage-like in appearance, consistent with a mechanical model of failure, but proponents of the film-rupture model continue to maintain that such surfaces can be reconciled with a dissolution failure mechanism. In particular, it is pointed out that faceted surfaces, similar in general appearance to cleavage surfaces, can be produced by active anodic dissolution. This suggestion is not consistent with our observations, based on studies of five different alloy systems, that the opposite transgranular

fracture surfaces are matching and interlocking, but nevertheless this view has continued to hold sway both in the U.S. and elsewhere.

Our recent studies on Admiralty Metal have provided considerable support for the mechanical school, and, conversely, has strongly challenged the dissolution proponents. Detailed fractographic studies of monocrystals established that the fracture surfaces consist of parallel {110} facets separated by surface steps. A difficulty in interpreting such fractographic detail has been uncertainty in relating the various features to the position of the crack front. In our work, this was overcome by the application of a series of load pulses during crack propagation which, by virtue of the increased plastic strain, marked the instantaneous positions of the crack front on the fracture faces. By varying the time intervals between pulses, the spacing between the crack-front markings was changed, providing useful information on the crack velocity. However, the most important result of this sample technique was that it established that the surface steps are approximately perpendicular to the crack front in all cases, and are thus analogous to cleavage steps in conventional brittle fracture.

In a related series of experiments, the environmental conditions during cracking were chosen to produce isolated regions of active anodic dissolution, juxtapositioned against the {110} stress-corrosion facets. Using a photogrammetric technique developed in our group, it was possible to show unambiguously that the dissolution facets were of {111} orientation, as would be expected for FCC material, and thus quite distinguishable from those produced by SCC. The dissolution facets were not matching on opposing fracture faces, again in contrast to the stress-corrosion fracture surfaces.

These and related experiments were presented at two major conferences on SCC in 1977, and made considerable impact. The characterization of the transgranular surfaces is now sufficiently complete that they can no longer be dismissed by general arguments but require specific interpretation. The surfaces are fully consistent with the mechanical (cleavage) models but no satisfactory explanations have been put forward by advocates of dissolution models. This research is focussing attention on what we consider to be the real question--the cause of the environmentally-induced brittle fracture.

Other Results: It was seen in preceding sections that there is considerable interest in the possibility that T-SCC is a form of HE. Our previous work in several materials, e.g., austenitic stainless steels, Mg-Al, Ti-Al and Al-Zn-Mg, has supported this view by confirming that these alloys can in fact be embrittled by hydrogen, introduced either by cathodic charging or from gaseous atmospheres. During the past year, this approach has been extended to Admiralty Metal and, in contrast to the other materials, our experiments have provided no evidence for any susceptibility to HE. These experiments do not rule out the possible involvement of hydrogen under the specific conditions which obtain during SCC, but nevertheless cause us to regard the hydrogen model with increased caution.

Expected Results FY79: Our previous studies of the SCC of the "near-alpha" Ti-8Al-1Mo-1V alloy have led us to conclude that it is a form of HE, and the final phase of this investigation is concerned with the specific role of hydrogen. In the case of gaseous HE, we have demonstrated that slow crack growth follows the α - β interface and occurs by the repeated formation and rupture of titanium hydride, as suggested by H. G. Nelson; we have shown that the hydride is readily detectable on the resulting fracture surfaces. In contrast, both internal HE and SCC (in aqueous chlorides) have been found to proceed by discontinuous cleavage through the α -phase, and attempts to identify hydride at the fracture faces have so far been unsuccessful. The change in fracture path can be rationalized in terms of differences in hydrogen fugacity in the different cases, but the possible absence of hydride raises serious questions about the underlying mechanism. We are presently intensifying our efforts to detect the hydride on stress-corrosion fracture surfaces, using essentially the same electron-diffraction techniques employed in the case of GHe, and anticipate resolving this issue in the coming months. X-ray diffraction or other methods will be employed if the electron-diffraction techniques prove inconclusive.

Another set of experiments has been undertaken during the past year which promises to yield results in FY79. These are being carried out on alpha-phase Cu-Zn alloys in aqueous ammonia, but bear on the general issue of the mechanism of I-SCC. The general consensus at the present time is that, with few exceptions, intergranular failures occur by the film-rupture model, outlined above, but the evidence for this view is far from conclusive. In Cu-30 Zn, I-SCC occurs in ammoniacal solutions which cause the formation of a cuprous-oxide passive film, commonly referred to as the "tarnish"; this failure corresponds to the well-known service failure, season-cracking. This alloy also undergoes SCC in ammoniacal solutions which produce active anodic dissolution in the absence of protective surface films, but in this case failure is the transgranular cleavage-like type, discussed above for Admiralty Metal. In our previous studies of acoustic emission during both modes of crack propagation, it was shown that the transgranular form was associated with a series of discrete signals of large amplitude, considered to correspond to the discontinuous advance of the brittle crack, while intergranular cracking produced virtually no detectable emissions. The latter is consistent with a purely dissolution-type mechanism, and thus these experiments support the film-rupture model for the intergranular case.

The situation in the brass-ammonia system is complicated by observations on the effects of zinc content on the characteristics of cracking. In tarnishing solutions, i.e., those which produce the cuprous-oxide film, cracking of alpha alloys is intergranular for all zinc concentrations, but for non-tarnishing solutions failure is transgranular for alloys containing less than 18% Zn and intergranular for those of lower zinc content. This transition in crack path at 18% Zn corresponds to a change in the dislocation structure of the deformed material from cellular to coplanar, attributed to the influence of zinc on the stacking-fault energy and hence on cross-slip. These observations suggest that two different forms of I-SCC

can occur in this system, the film-rupture mechanism in tarnishing media and a mechanical type for alloys with less than 18% Zn tested in non-tarnishing solutions. The latter may occur by basically the same mechanism as in the T-SCC of Cu-30 Zn and Admiralty Metal, the change in crack path being associated with the change in dislocation behavior.

The possible occurrence of two fundamentally different mechanisms of I-SCC has considerable general relevance since it suggests the possibility that cases of I-SCC in other systems may not involve the film-rupture mechanism as is commonly assumed. To pursue this possibility, crack-propagation studies are in progress on a high-purity Cu-10% Zn alloy tested in both tarnishing and non-tarnishing solutions. The acoustic emission is being monitored, and a comparison will also be made of the intergranular fracture surfaces produced in the two cases. By analogy with the transgranular failures in Cu-30 Zn and Admiralty Metal, it might be expected that failures in the non-tarnishing case would yield discrete emissions, and would show evidence of crack-arrest markings on the fracture surfaces, resulting from discontinuous crack advance. The intergranular failure in the tarnishing case is expected to resemble that for Cu-30 Zn in the same solution, discussed above.

During the past year, a study has been initiated of the formation of the cuprous-oxide passive film on alpha-phase Cu-Zn alloys in tarnishing ammonia solutions. Earlier work sponsored by ARO indicated that the susceptibility of these alloys to I-SCC increases with increasing zinc content, and that this effect is probably related to the influence of the alloying element on the passivation process. Ellipsometric studies of unstressed specimens in 1N solutions established that the cuprous-oxide film grows to a limiting thickness of ~ 250 Å and that the zinc content has no significant effect on the growth kinetics. Rather, zinc appears to accelerate the subsequent breakdown of the film and the present studies are focussing on this aspect, employing the SEM and the TEM replica technique. The breakdown process will also be studied by cathodically reducing the film and examining the underlying metal, and by various techniques which decorate breakdown sites. Studies will be conducted on specific single-crystal planes and on polycrystals. Particular attention will be given to the role of grain boundaries in the breakdown process.

In addition to binary Cu-Zn alloys, experiments will be carried out on Admiralty-Metal polycrystals. The presence of the additional alloying elements in this alloy, which consists of Cu-29 Zn-1Sn plus small amounts of antimony and arsenic, considerably reduces the susceptibility to I-SCC, and thus we expect to observe a significant difference in grain-boundary attack in this alloy. It is possible that Auger spectroscopy will be used to determine the distribution of the alloying elements.

While these studies are motivated by our interest in I-SCC, it should be noted that the breakdown of passivity, e.g., pitting, is a subject of great practical and scientific interest in its own right, and is being studied on campus by R. C. Alkire and, independently, by M. Metzger. It is hoped that a significant thrust will be developed in this area.

Expected Results FY80: It has been our intent that the studies of the transgranular cleavage-like failures should move increasingly towards the use of the TEM and other electron-optical techniques to identify the embrittling phase. Because of experimental difficulties and to some extent because of students' interest, this stage has not advanced as quickly as planned, but useful data should be obtained in FY79 and certainly in FY80. These studies will be carried out in collaboration with H. L. Fraser on Mg-Al, zircaloy, Admiralty Metal and possibly austenitic stainless steel. In the magnesium alloy, our previous DOE work indicated that both SCC and HE are associated with the formation of surface layers of MgH_2 , and the TEM studies are designed to obtain a more detailed knowledge of the structure and morphology of the hydride. It is hoped that these studies will resolve several apparent anomalies which currently exist. For example, SCC in this alloy occurs by cleavage on {3140} planes, whereas IHE and GHE produce transgranular fracture surfaces which are uneven on a microscopic scale, exhibiting a corrugated appearance, and which do not tend to lie in {3140} planes. It may be speculated that these differences result because fracture in SCC occurs on the cleavage plane of a thick hydride, but that the processes involve cracking along the habit planes of thin plates.

In the zircaloy, our experiments are related to the embrittlement which occurs in iodine vapors at elevated temperatures. This is a transgranular failure which has occurred in zircaloy fuel cladding, iodine being a fission product, but the prime motivation for our work is mechanistic and relates to HE. The characteristics of HE and iodine embrittlement are closely similar, and thus further insight into HE may be obtained from studies of the latter since, in contrast to hydrogen, iodine can be detected by electron-optical techniques such as Auger spectroscopy and the microprobe.

For each of the alloys, a difficult yet important technique will involve the direct examination of the fracture surfaces with the TEM, preparing foils by thinning from behind the fracture face. If successful, such studies should yield information on the structure and composition at the fracture surfaces, and hence provide valuable insight into the embrittlement process.

It is more difficult to anticipate the direction of our future work on I-SCC since this will depend on the outcome of the present work. In Cu-30 Zn, evidence obtained to date is consistent with the film-rupture model, and thus effort should continue on the passivation and, more particularly, on the breakdown of passivity at grain boundaries. This is a difficult problem experimentally since it is necessary to correlate the corrosion and stress-corrosion behavior with the composition at the grain-boundary regions. The latter is difficult to obtain. The problem can be attacked by Auger spectroscopy but requires that intergranular surfaces be produced in the chamber of the instrument, an extremely difficult task in ductile materials. Another approach is via analytical electron microscopy, using a scanning transmission electron microscope (STEM) in conjunction with both x-ray and energy-loss

spectroscopy. This technique promises to permit the analysis of regions ~ 100 Å wide and thus may prove suitable for grain-boundary studies. In this regard, it should be noted that the MRL has recently acquired a new STEM, a V6HB5, which is the most advanced instrument available for analytical electron microscopy at the present time.

It was seen (above) that there is some uncertainty about the generality of the film-rupture mechanism in practical cases of I-SCC. Depending on the outcome of the current acoustic-emission and fractographic studies of Cu-10 Zn, it may be desirable to extend this work to characterize other cases of I-SCC.

Relationship to Other Projects: As stated above, the program is part of a broad study of SCC and HE on the Urbana-Champaign campus. Thus the Principal Investigator, sharing a postdoctoral fellow with C. J. Altstetter, is taking part in a NSF-funded study of SCC and HE of austenitic stainless steels; this is part of a larger, interactive program on the HE of Fe-Ni-Cr alloys (with H. K. Birnbaum and H. L. Fraser). The International Nickel Company recently provided a fellowship to support additional work on the embrittlement of the austenitic stainless steels. The Principal Investigator and R. A. Yeske, formerly a MRL member but now at Westinghouse Research and Development Center, are conducting an AFOSR-supported program on the I-SCC of Al alloys. This program emphasizes the fracture-mechanics approach to the characterization of crack propagation, and aims to correlate the velocity of I-SCC with microstructure and with hydrogen permeation. The phenomenon of HE is also being studied by H. K. Birnbaum in niobium, and there is useful interaction between this work and our DOE program.

The addition of R. C. Alkire to the DOE program is particularly encouraging. Part of his program deals with the breakdown of passivity by fluid-flow processes, and thus there is common ground with our studies of I-SCC, as noted above. There has been good interaction in the past, mainly involving exchange of equipment and collaboration in teaching in the corrosion area, but it is hoped that our MRL-DOE association will lead to more direct cooperation in our respective research efforts.

It is fair to say that a significant thrust is being developed in the area of environmentally-induced fracture. To date, there has been no difficulty in avoiding overlap between the DOE and other programs since they have been differentiated both by the materials studied and by the main experimental techniques, and we do not anticipate that this will become a problem.

Publications (Calendar Year 1977):

G. H. Koch, A. J. Bursle, and E. N. Pugh
Gaseous Hydrogen Embrittlement of Ti-8Al-1Mo-1V
Proceedings of the Second International Congress on Hydrogen in Metals,
France, 1977 (Pergamon, 1977), 3F5.

G. H. Koch, A. J. Bursle, and E. N. Pugh
Comparison and Interpretation of Fracture Surfaces Produced in
Ti-8Al-1Mo-1V by Stress-Corrosion Cracking and Slow-Strain-Rate
Hydrogen Embrittlement
Metall. Trans. 9A, 129-131 (1978)

A. J. Bursle and E. N. Pugh
On the Mechanism of Transgranular Stress-Corrosion Cracking
Proceedings of the Conference on Mechanisms of Environment Sensitive
Cracking of Materials, England, 1977, Metals Society (in press)
Also supported by National Science Foundation DMR 74-24648

M. S. Theses (Calendar Year 1977):

None

Ph.D. Thesis (Calendar Year 1977):

John Alvin Beavers (E. N. Pugh, adviser)
Stress Corrosion Cracking of Admiralty Metals in Aqueous Ammonia
1977
Also supported by the U. S. Army Research Office (Durham)

AK-01-02-01-3 Physical PropertiesMechanical Properties of Solids

Principal Investigator: Jon T. Holder, Ph.D.
Associate Professor of Geology

Supporting Agency: U. S. Department of Energy

Senior Staff: Jon T. Holder, Associate Professor

Junior Staff: Theodore A. Koelsch, Research Assistant
Sekyung Lee, Research Assistant
Jerry Sweeney, Teaching Assistant

Object: This project is concerned with the investigation of microscopic processes which affect the mechanical properties of solids. The studies are generally carried out in relatively simple systems in an attempt to better understand mechanical behavior in more complex natural systems. Measurements often involve ultrasonic techniques. Current efforts are concentrated on dislocation dynamics in crystalline ice and deformation mechanisms in geologic systems. We are also actively collaborating with A. V. Granato in an ultrasonic investigation of point defect behavior in irradiated metal crystals.

Dislocation motion in ice is limited by the very large intrinsic, linear viscous drag rather than by more complex thermally activated point-defect dislocation interactions and our initial study of plastic flow in predeformed ice crystals established that macroscopic deformation can, in some cases, be described analytically in terms of the microscopic dislocation motion. Our continuing investigation of dislocation dynamics makes use of these unique features of ice, in two experimental approaches: 1) the motion of low angle tilt boundaries is limited by the same large viscous force that limits microscopic motion, and the motion of these boundaries is optically observed continuously during the deformation of samples; 2) the dislocation density in samples predeformed to a relatively high stress level remains approximately constant during subsequent measurement at low stress levels, and the measured microstrain behavior of these samples provides direct information about dislocation velocities during the tests. Currently the first approach is being used to investigate the interactions between dislocation segments and point obstacles at the segment ends, and the effects of dissolved impurities such as HF on the dislocation motion. The measurements are supplemented with conventional internal friction measurements on both pure and HF doped samples. The results of this study and their comparison with calculated results should lead to a better understanding of the mechanisms responsible for the large intrinsic viscous drag on the dislocation. In addition, the tilt boundary studies in samples with point obstacles represent the first continuous direct observation of the dynamics of pinned dislocation segments, and the results may be of use in the more general area of plastic flow.

The objective of the study of deformations in geologic materials is the determination of the relative importance of processes such as intragranular

and cataclastic microfracture, twinning and dislocation glide, and grain boundary sliding in the process of deformation under various environmental conditions. The approach being used is the simultaneous measurement of acoustic emissions generated in the 10 KHz - 1 MHz range, ultrasonic velocity changes, macroscopic dilatency of the sample, and axial strain during the laboratory deformation of natural rock specimens. Supplementary studies are also carried out for single crystal deformations. The principal emphasis is initially concerned with the analysis of the pulse shape, amplitude, and frequency content of the acoustic emissions generated by different deformation mechanisms. Knowledge of this sort will be of use in continuous monitoring of deformation processes in laboratory deformations, and has potential for use in field application. For example, the results could be important in analyzing seismic activity and velocity determinations for considerations of radioactive waste disposal sites, or for consideration of geothermal energy generation in areas where rock porosity is to be increased by fluid injection.

The study of irradiation-produced defects in metals is the primary concern of the research project of A. V. Granato, but I maintain an active role in that study. In addition to some direct support in equipment funds, I contribute to the study in a number of ways. The project is largely based on the results of a previous collaboration between Professor Granato, one of my graduate students, Oak Ridge National Laboratory, and myself, which demonstrated the power of ultrasonic techniques in studying point defect geometry and dynamics. I have been particularly involved in the development of the very high resolution velocity measurement techniques necessary for this type of measurement. Details of the scope and projected results of this project are described in the proposal of Professor Granato.

One other investigation is still continuing on a reduced scale concerning structural phase stability in alkali halides. The work is largely confined to publication of the studies carried out in FY75 and 76, but some new aspects are still being considered. This consideration is based on observations in the earlier nonhydrostatic phase stability and third order elastic constant measurement and calculations, which indicate that values for parameters in widely used Born-model interatomic potentials should be reevaluated.

Results FY78:

Most Significant Accomplishments: Measurements have been largely completed on the motion of low angle tilt boundaries in ice crystals containing inclusions which serve as point obstacles to the ends of the boundaries. In this system, the dislocation-inclusion interaction, as well as the behavior of pinned dislocation segments, could be observed optically during deformation by applied stress. To our knowledge these are the only continuous observations of bowing dislocation loops during deformation. The results indicate that dislocation motion is slowed considerably more than expected by the process of bowing out, and the absence of significant recovery after stress removal demonstrates that the effect is not related to an anomalously large dislocation line tension. Measurements were also carried out

for numerous sample and tilt boundary geometries, and the consistency of the results indicate that the contributions from sample geometry and surface effects are negligible. An attempt will be made during the remainder of FY78 to analyze the results by comparison with model calculations, and it is hoped that the experimental results can be used to understand the detailed nature of the dislocation dynamics in ice.

Other Results: Acoustic emission measurements have been carried out for single crystals of calcite in order to supplement the previous data from natural rock specimens. An interface system has been set up to Fourier analyze the acoustic emission signals, which are stored on video tape. This analysis will be used to design filter systems to separate different types of signals which can be associated with specific deformation mechanisms. In order to further delineate the deformation processes taking place during the laboratory deformation, facilities for simultaneous ultrasonic velocity and dilatancy measurement are being added to the system.

Preliminary ultrasonic velocity and attenuation measurements have been carried out with the gated-carrier interferimetric system constructed during the last fiscal year, during and after electron irradiation of Al-Zn and Al-Mn alloys. This initial study of self-interstitial-impurity defect complexes in Al, in collaboration with Professor A. V. Granato, is expected to be completed during FY78.

A computer calculation of Born model parameters in alkali halides has been initiated. The study is the result of our earlier studies of phase stability and third order elasticity in rubidium halides, in which it was found that with the recently calculated van der Waals parameters the analytic Born model could account for the static lattice properties more successfully than had previously been supposed.

The results of the initial study of plastic flow in predeformed ice crystals were presented at the International Symposium on the Physics and Chemistry of Ice, Cambridge, England. Our study of dislocation dynamics in ice will be presented as an invited talk (Symposium on Unusual Dislocation Behavior, American Physical Society meeting, March 1978, Washington, D. C.).

Expected Results FY79: We hope to continue the study of dislocation motion in ice with a new project beginning in late FY78. This study will be directed toward two problems of dislocation behavior: 1) the nature of observed recoverable dislocation contributions to plastic strain; and 2) the relative importance of stress induced ordering of water molecules and proton disorder along the dislocation core to the large viscous drag on dislocations. The study will probably utilize measurements on predeformed samples, as a function of the concentration of HF, hydrostatic pressure, and perhaps NaCl. Besides the direct implications for mechanical behavior of sea ice, the effects of NaCl are of interest because of its apparent role in producing microscopic pinning points for dislocation segments.

The initial project of rock deformation studies will continue into FY79. This study is primarily directed toward the development of ultrasonic

and acoustic emission techniques in monitoring the deformation mechanisms, and new studies involving their application to specific problems should be undertaken by FY79. The most likely systems to be studied are: 1) the anomalous increase in strength of limestone with increasing temperature; and 2) the relative importance of chemical and mechanical processes in hydrothermal porosity increases in limestone-fluid systems at high temperature and pressure. Both of these studies may have direct energy-related implications in relation to the consideration of limestone deposits as potential radioactive waste disposal sites.

The acoustic emission studies in this project may also be supplemented by a study being set up at the Rhine-Westfahl. Technische Hochschule, Aachen, West Germany. During my sabbatical there, during the fall of 1977, a program for acoustic emission study of the relative importance of twinning and dislocation glide for the deformation of single crystals of zincblende was initiated, in collaboration with Professor H. Siemes. The results from that very simple and relatively well-understood system should be very useful in understanding the nature and sources of acoustic emission generated in more complex rock systems being studied here.

The collaboration with Professor Granato on ultrasonic studies of point defects in metals will continue into FY79 and I anticipate that my involvement will increase. A large portion of my time during my sabbatical last fall was spent in the Institute for Metal Physics at the Technische Hochschule Aachen, in connection with their ultrasonic velocity and attenuating studies of defects in copper. The measurement system for this project is in operation and the initial project should be completed within FY78. It is expected that this system can be used for the study of a number of point-defect, self-interstitial systems in metals, beginning in FY78 and extending through FY79. In addition, I hope to be able to pursue the investigation of long range point defect-dislocation interactions undertaken while in Aachen. This study has been of interest to Professor Granato for some time, and involves in principle the same stress induced ordering mechanisms proposed for the large dislocation drag in ice.

A calculation of repulsive parameters for atomic interactions in alkali halides, using recently reported large values of van der Waals parameters, is also being considered for FY78-79.

Expected Results FY80: The expected work during this year will primarily be the continuation of projects started in FY79, in the three areas of plastic flow in ice, rock deformation, and radiation damage in metals. There are several new areas of potential research still being considered, which could begin in late FY79 or 80. These include studies of plastic flow in single crystals of other important geologic systems, and the application of the ultrasonic rock deformation analysis to igneous rocks, which have much greater mechanical strength than materials such as limestones, marbles, and sandstones presently being studied. Other plastic flow systems of interest are salt, where input data is needed for modeling of deformation behavior for radioactive waste disposal sites, and upper

mantle material in which very large viscous drag on dislocations may result in relatively simple mechanical behavior such as that found for ice. Acoustic emission studies in igneous materials would have more direct energy-related implications because of their importance in geothermal energy production.

Relationship to Other Projects: My involvement with the MRL enables me to utilize my background in solid state physics to a considerably greater extent than would otherwise be possible. The collaboration with A. V. Granato on ultrasonic measurements of point defect structure provides a means for continued participation and contribution to the important field of metal physics, in which I have been active since my graduate training. The same ultrasonic techniques are used in other geophysical areas of research so that the interaction is beneficial indirectly as well. In addition to Professor Granato, this study involves much interaction with J. S. Koehler. A joint seminar topics of point defect behavior in metals, involving the participation of Professors Granato, Koehler, their graduate students, postdoctorals, and myself was conducted during spring and summer of 1976.

Professor Granato also interacts strongly with the mechanical property of ice investigation. He was a collaborator in the initial study of plastic flow in ice, and maintains an active interest in the current study. Continuous contact has been maintained with Dr. K. Itagaki of the U. S. Army Cold Regions Research and Engineering Laboratory, who has provided a number of important suggestions. Although this interaction has been fairly loose in the past, several communications have been involved during the current year, including a visit to the MRL by Dr. Itagaki.

The studies of rock deformation are carried out in cooperation with, and utilizing the high pressure apparatus of Professor F. A. Donath (Geology). His principal research support is from private petroleum companies, and the implications of this study to hydrocarbon deposits is under continuous scrutiny. Professor Donath serves on an American Physical Society panel investigating radioactive waste disposal, and the utilization of results from our study in site evaluation and monitoring are continuously being considered.

This rock deformation project has involved numerous consultations with Professor E. N. Pugh, whose work in metallurgy involves the use and interpretation of acoustic emissions. We have also interacted with Prof. F. V. Lawrence (Civil Engineering), whose research has concerned acoustic emissions in geologic and engineering material. That interaction involves the use of some of his equipment as well as numerous discussions concerning measurement techniques and microscopic emission source mechanisms.

Our project interacts strongly with another study which indirectly involves federal funds: the investigation of mechanical and dielectric anisotropies in naturally deformed slates, being carried out by Professor D. S. Wood (Geology). We are actively involved in the ultrasonic and dielectric measurements carried out in that study, which utilize some of our MRL

equipment. Our principal concern has been with the mechanisms responsible for the anisotropies and our discussions have also frequently involved Professor D. A. Payne concerning the dielectric response of heterogeneous aggregates. The concepts of this project are presently being studied by coal geologists at the Illinois State Geologic Survey under an ERDA grant, in hopes of utilizing them in exploration techniques. We are consulting with the graduate student responsible for setting up their initial laboratory ultrasonic studies of shales.

Publications (Calendar Year 1977):

R. J. Wallat and J. Holder

Third Order Elastic Constants of Rubidium Chloride

J. Phys. Chem. Solids 38, 1227-1231 (1977)

Supported by National Science Foundation DMR 76-01058

D. M. Joncich, A. V. Granato, and J. Holder

A Direct Determination of an Upper Limit for the Electrical Charge on Dislocations in Ice

J. Glaciology (accepted for publication)

Supported by National Science Foundation DMR 76-01058

R. J. Wallat and J. Holder

The Born Model and the Effects of Hydrostatic and Non-Hydrostatic Stresses on Rubidium Halide Structural Phase Transitions

Phys. Chem. Solids (accepted for publication)

Supported by National Science Foundation DMR 76-01058

Theses (Calendar Year 1977):

None

Dielectric Solids

Principal Investigator: David A. Payne, Ph.D.
Assistant Professor of Ceramic Engineering

Supporting Agency: U. S. Department of Energy

Senior Staff: David A. Payne, Assistant Professor

Junior Staff: William L. Streicher, Research Assistant
Bruce A. Tuttle, Research Assistant

Object: The dielectric solids research program is concerned with the synthesis, preparation, crystal growth, fabrication, characterization and property measurements on new and improved ceramic materials suitable for energy conversion and detection systems. It is principally concerned with structure-property relations in acentric polar oxides, and the relationship between intrinsic single crystal properties with polycrystalline properties that are often influenced by extrinsic microstructural features. Out of this work has grown the concept of microstructural engineering, and how properties may be optimized in polyphasic systems through the proper use of mixing rules. In some cases, properties are attained which are strictly a function of polycrystallinity alone, and which could never be realized in single crystal systems (e.g., recomensated internal boundary layer dielectrics, positive temperature coefficient of resistance thermistors, high voltage varistors). It should be noted that many of the highly polar materials exhibit a disruptive phase transformation on cooling from the high temperature prototypic state, and thus considerable effort has been spent on reduced temperature crystal growth, liquid phase sintering and hot-pressing.

With respect to energy related applications, piezoelectrics may be used to transduce mechanical work into electric potential, or vice versa; pyroelectrics for the conversion of thermal fluctuations into electric current; and highly susceptible ferroelectrics for storage of electric energy. Materials currently being investigated include: (i) Bi_2WO_6 , a two-dimensional layered compound, which, from crystal physics considerations, should be a high efficiency piezoelectric; (ii) $\text{Pb}_5\text{Ge}_3\text{O}_{11}$, an optically active pyroelectric, whose nucleation and growth behavior from splat-cooled glasses is being investigated in an applied electric field (with a view to aligning polar axes parallel to incident energy for large surface area solar coatings); (iii) high permittivity dielectric mixtures (BaTiO_3 - $\text{Pb}_5\text{Ge}_3\text{O}_{11}$, PbTiO_3 - $\text{Pb}_5\text{Ge}_3\text{O}_{11}$) for energy storage; and (iv) semi-conducting perovskites (chemically doped SrTiO_3 , BaTiO_3) for thermal sensors, current limiters and electrodes for photoassisted electrolysis of water for hydrogen fuel.

The long term trend will concentrate on ceramic materials for solar energy. In all likelihood, the research will be concerned with the basic choice of materials and associated material limitations. Examples should include: (i) direct dielectric power conversion of waste heat into electricity using ferroelectric solid state heat engines (based upon pyroelectric discharge and electrocaloric cooling),

and (ii) spontaneous decomposition of water, using photoassisted electrolysis and semiconducting perovskite electrodes.

Results FY78:

Most Significant Accomplishments: (1) For the first time, Bi_2WO_6 was grown in cm size crystals by flux growth, and large polycrystalline specimens fabricated in dense forms by hot-pressing techniques.

Single crystal Bi_2WO_6 was grown by the flux method at temperatures significantly below the polymorphic transformation temperature. A number of fluxes were investigated (LiCl , KF , PbO , V_2O_5 , Bi_2O_3), but emphasis was placed on Bi_2O_3 since it alone did not contaminate the crystals. The ternary system B_2O_3 - Bi_2O_3 - WO_3 was investigated by a combination of techniques which included differential thermal analysis and hot-stage microscopy. Both melting and crystallization temperatures were identified, and melt surfaces observed for the separation of crystal phases. For the optimum composition, crystals grew in a temperature gradient of $10^\circ\text{C}/\text{cm}$ within a vertical tube furnace, with the bottom of the crucible being hotter than the melt surface. Thicker crystals were grown at lower cooling rates ($1^\circ\text{C}/\text{min}$), and visually it was verified that nucleation started in the center of the melt surface with growth occurring towards the crucible wall.

Additions of B_2O_3 (0-80 mol%) substantially increased the phase field of Bi_2WO_6 towards lower temperatures. Three distinct regions were observed: Region I (0-30 mol% B_2O_3), homogeneous melt formation with solidification of very fine crystallites; Region II (30-50 mol% B_2O_3), surface nucleation of Bi_2WO_6 , and under favorable conditions, growth of large cm diameter crystals; Region III (> 50 mol% B_2O_3), liquid-liquid immiscibility. The most favorable composition for Bi_2WO_6 growth was 40% B_2O_3 - 50% Bi_2O_3 - 10% WO_3 . Differential thermal analysis of this prereacted composition indicated a melting endotherm at 640°C and an extended crystallization exotherm between 790 and 890°C .

Optically clear single crystals were examined under cross polarized light on a hot-stage microscope. The plates were placed on a sapphire substrate whose optic axis was parallel to the optic axis of the microscope. Optical retardation was measured by using a calibrated quartz wedge. Temperature control was excellent, and temperatures could easily be changed by 1 to 2°C increments within the transformation range. Precise temperatures were known by calibration against the melting points of known salts and metals. Domain nucleation started at 975°C but proceeded at an exceedingly slow rate. As the temperature was increased slowly, the domains grew at 90° to one another. At 985°C , localized areas within the polydomains exhibited extinction, resulting in patchy structures. The transformation proceeded and was completed by 1030°C when all the crystal was in extinction. A 45° rotation of the crystal brought back maximum transmission. Considerable hysteresis (> 100°C) in the phase transition was observed on slow cooling. The transition was not observed at 1030°C , and only at 1012° did cellular regions start to nucleate and grow. The cellular structure remained until 865°C , where upon extinction started in isolated regions. These dark

regions expanded and grew until complete extinction was observed by 815°C. Another 45° rotation of the crystal brought back transmission, which now was poor due to microcracking within the crystal. Cellular crack patterns, and cracks running parallel with the original domain walls were observed. Apparently, domain formation was insufficient to relieve transformational strain (tetragonal-orthorhombic), and elastic failure occurred along twin boundaries. On reheating, the retardation was the same with the only discontinuities occurring at 985°C on heating and 865°C on cooling. These transformations took place by 90° twinning. Identical observations have recently been made on thicker grown hydrothermal crystals.

The transition behavior has also been followed on polycrystalline samples by thermal expansion measurements. A recording dilatometer identified the onset of sintering at 700°C, which proceeded to approximately 950°C whereupon an expansion discontinuity occurred. The expansion (~ 3% linear strain) was sufficient to "de-sinter" the ceramic. Thermal hysteresis occurred again on cooling, with a slight contraction at 860-870°C, in excellent agreement with optical measurements. These findings indicate that fabrication of Bi_2WO_6 would have to occur at temperatures between 700-950°C, preferably closer to the upper limit. Unfortunately, isothermal shrinkage studies at 850-920°C indicate the sintering rate is exceedingly slow and dense compacts are never realized. Therefore, we have gone to hot-pressing techniques for the preparation of dense large samples suitable for dielectric applications. A hydraulic press, equipped with a split-tube furnace, protective cooling system, recording dilatometers, and alumina dies and punches was used. Dense compacts were fabricated at 850°C by the application of 500 Kg/cm² of uniaxial pressure for one hour. The microstructure exhibited a platelike morphology, but XRD measurements indicated a lack of preferential orientation. Dielectric measurements identified a dielectric anomaly at 380°C. Previous DTA measurements showed no transition at this temperature, but recent differential scanning calorimeter (DSC) measurements detected a diffuse enthalpy of "transition". Attempts are underway to quantify this transition, and investigate the applicability of internal stress mechanisms. Thermal history and repeated thermal cycling of the samples will be investigated.

2) The dielectric behavior of lead germanate glasses [$\text{Pb}_5(\text{GeSi})_3\text{O}_{11}$] formed by splat-cooling was investigated with novel results. The softening points, recrystallization temperatures and melting points were identified by DTA, and their enthalpies of transition determined by DSC. Dielectric and electrical conductivity measurements were made up to the melting points (~ 700°C) with an unexpected dielectric anomaly discovered as the glass restructured and crystallized, at temperatures (350-400°C) significantly above the Curie temperature. Ferroelectricity only developed after extended treatment at temperatures close to the melting point. Dielectric and ac conductivity measurements are being taken as a function of frequency (10^2 - 10^6 Hz), field and time, and a model is being developed to explain these anomalous behaviors. It is based upon structural reorganization within the glass, nucleation and growth of dispersed crystals, and crystal interpenetrations. An essential aim of the project is to control nucleation and growth in an applied electric field, so "poled" crystals

may be aligned parallel to incident energy in large surface area coatings, suitable for energy conversion and detection.

Other Results: (1) Microstructural engineering of optimized ferroelectric mixtures in the system $\text{BaTiO}_3 - \text{Pb}_5\text{Ge}_3\text{O}_{11}$ was completed with practical implications for the multilayer ceramic capacitor industry. Considerable savings can be realized in energy, refractories and electrode costs. Liquid phase sintering was used as a fabrication process to distribute a lower melting point second phase which aided densification through particle rearrangement and viscous flow. BaTiO_3 normally sinters at 1300°C and $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ melts at 740°C . Mixtures were sintered to end point density at 850°C . Direct observation of the rate of removal of pores led to a phenomenological theory of sintering based upon multiple pore size distributions and the preferential elimination of smaller pores with time at temperature. A materials characterization study was completed. Techniques employed, included wetting studies, DTA, XRD, SEM, EPMA, quantitative microscopy, dielectric analysis and electrical measurements.

(2) The investigation of interfacial impedance layers in polycrystalline zinc oxide based varistors was completed in FY77 which led to the design of improved electrical ceramics for high voltage protection. Dielectric dispersion analysis was used as a tool to probe the nature of electrical boundary conditions within polycrystalline ceramics. A brick-wall model was proposed and defended (through the use of appropriate equivalent circuits) as a representation of the microstructure of multibarrier ceramic varistors. The analysis was facilitated by the fabrication of single crystal bilayer devices by evaporating Bi_2O_3 thin films on zinc oxide single crystals of known resistivity. Analysis of the dielectric spectrum by Cole-Cole techniques indicated striking similarities between the properties of bilayer devices and multijunction varistors. Specifically, the magnitudes of the static dielectric constant, relaxation frequency and high frequency dielectric constant were in excellent agreement with Maxwell-Wagner theory.

Microstructural modeling of electrical ceramics has led to an investigation of the possible control of resistivity distributions within ceramic perovskites. Past work on aliovalent doping of BaTiO_3 has now been extended to the chemical recompensation of insulating boundary layers within semiconducting SrTiO_3 . The subsequent formation of internal boundary layer capacitors gives rise to an apparent enhancement of the geometric dielectric constant to values $> 20,000$ with loss tangents < 0.03 . Since SrTiO_3 is a near linear paraelectric at room temperature, this new type of high capacitance ceramic is extremely stable with respect to temperature, field and time, when compared to high permittivity ferroelectric materials. It now offers the possibility of stable electrostrictive transduction of energy.

Results Expected FY79:

We plan to conclude our work on Bi_2WO_6 and $\text{Pb}_5(\text{Ge},\text{Si})_3\text{O}_{11}$. With respect to Bi_2WO_6 , high temperature XRD measurements will be taken of the phase transition behavior. The lower transitions will be investigated in more detail. Attempts

will be made to develop orientated microstructures for maximum electromechanical response. Hot extrusion is one method of proposed pressure assisted fabrication. With respect to $\text{Pb}_5(\text{Ge,Si})_3\text{O}_{11}$, a model will be derived to explain the anomalous dielectric response as the glass restructures and recrystallizes.

We expect to continue our work on crystal growth of polar materials and develop the capability of top-seeded flux pulling. The characterization technique of second harmonic generation (SHG) in acentric solids will be introduced for evaluation of new materials suitable for energy conversion applications. The ferroelectric behavior of polycrystalline NaNbO_3 (which in single crystal form is antiferroelectric) will be examined, and a thermodynamic analysis formulated to determine if anisotropic grain boundary stress is sufficient to modify the properties of polarizable deformable solids. This model will be adapted to members of the bismuth titanate family of materials.

Microstructural engineering of diphasic dielectric mixtures by liquid-phase sintering techniques will be extended further to the system $\text{PbTiO}_3\text{-Pb}_5\text{Ge}_3\text{O}_{11}$. Lead titanate transducers are difficult to fabricate into dense strong forms, but are extremely important for piezoelectric applications. We expect to make an important contribution in this area. In addition, Curie-Weiss analysis will be developed further to quantify reaction kinetics between ferroelectric mixtures. Curie-Weiss analysis is a new technique, which is several orders of magnitude more sensitive than x-ray diffraction.

The electric and dielectric nature of grain and phase boundaries in electrical ceramics will be investigated further. We plan to use Auger spectrometry to determine depletion layer depths at interfaces in varistors and thermistors, and correlate this information with calculated values from impedance measurements. The purpose of this work is to obtain a more fundamental understanding of the role of microstructure upon electrical properties and develop the concept of microstructural engineering for property optimization in energy-related materials.

Results Expected FY80:

In the years ahead, we plan to concentrate more on the choice of ceramic materials for solar energy applications. Basic considerations will be given to (i) dielectric power conversion, and (ii) photoassisted electrolysis of water. Many of the candidate materials are perovskites, and we have had considerable experience in the past on how to fabricate these materials for the development of optimum properties. An example would be the chemical doping of SrTiO_3 for semiconducting electrodes, which should be more stable than the current materials used in optical-chemical conversion.

With respect to dielectric power conversion, we plan to carry out a complete thermodynamic analysis of the proposed Carnot cycle using Gibbs free energy functions. Previous workers have not included stress-strain terms which could be significant in polycrystalline ferroelectrics. The pyroelectric and electrocaloric

effects will be influenced by residual transformational stress in bonded crystallites through the piezoelectric effect, and thus the Carnot efficiency may be optimized for particular microstructures, when domain size to grain size ratios are taken into consideration. We plan to continue our work on PbTiO_3 - $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ mixtures, since a continuously connected $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ ferroelectric intergranular phase, distributed by liquid phase sintering, would maintain a high volume spontaneous polarization, but would decrease the apparent dielectric constant of the mixture (κ) by placing low permittivity ($\epsilon_2' = 40$) paths in series with flux passage. This is needed to maximize the pyroelectric efficiency. Thus, it may be possible to microstructurally engineer a diphasic ferroelectric power converter with high $\bar{P}_s$ and low $\bar{\kappa}$ in polycrystalline form, which could not be possible by any other method, including single crystals. We propose to investigate this aspect of materials optimization for efficient thermal-electric conversion.

With respect to photoassisted electrolysis, we plan to investigate basic crystal chemical aspects of the choice of electrode materials (e.g., band gaps, electron affinity, quantum efficiency) and the influence of surface salts on electrochemical processes and spectral response.

Relationship to Other Projects:

The crystal growth and characterization studies are related to other materials research projects within this Laboratory as are the microstructural modeling and property determinations of layered compounds. We have entered into a collaboration with the Center for Energy and Environment of the Department of Energy at the University of Puerto Rico on crystal growth, ceramic fabrication and dielectric measurements on ferroelectric compounds within the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ family of layered materials. Under separate contract, ER-78-S-02-4679, we have recently agreed to advise Power Conversion Technology, Inc. of LaJolla, California, on the choice of ferroelectric materials for solid state heat engines and carry out property measurements to assess the feasibility of efficient power conversion.

Publications (Calendar Year 1977):

D. A. Payne and L. E. Cross

Microstructure-Property Relations for Dielectric Ceramics:

I. Mixing of Isotropic Homogeneous Linear Dielectrics
Ceramic Microstructures '76 (Westview Press, 1977), pp. 584-597

D. A. Payne

Processing of Crystalline Dielectrics for Ceramic Capacitors
1977 University Conference on Ceramic Science (Plenum Press, in press)

Theses (Calendar Year 1977):

S. M. Park (D. A. Payne, Adviser)

Liquid Phase Sintering of Heterophasic Dielectrics in the System BaTiO_3 - $\text{Pb}_5\text{Ge}_3\text{O}_{11}$
 Ph.D. Thesis

Nuclear Magnetic Resonance Studies of Metals and Polymers

Principal Investigator: Theodore J. Rowland, Ph.D.
Professor of Physical Metallurgy

Supporting Agency: U. S. Department of Energy

Senior Staff: Theodore J. Rowland, Professor

Junior Staff: Patrick Lenahan, Research Assistant

Object: Presently we are successfully investigating the electronic properties and structure of the organic semiconductors A and its very close homologue P. Only a few such compounds with one-dimensional molecular structure have been identified and their electronic properties are interesting and unusual. Our attention was drawn to these particular compounds by the results of earlier studies focusing on their large optical absorption in the visible and infrared, their carrier lifetime, and electron spin resonance. As a new class of materials, their properties must be investigated to determine their value for future solid state device use. In addition, we believe the possibility exists of forming from these compounds a junction which would serve as a prototype photovoltaic converter. In their direction of best electrical conductivity, the compounds A and P both have the characteristics required of candidates for photoelectric conversion. In addition, there are other electronically active compounds of the form $R(TCNQ)_x$ which are different chemically, yet whose R molecules are sufficiently similar in size and shape that their crystal structure differs only slightly from A and P. Here, we foresee the possibility of marked changes in property with the formation of dilute solid solutions. Our crystal growing techniques are thoroughly developed; we have no reason to doubt that the material we are investigating, both in single crystal and polycrystalline form, is not the purest and most carefully synthesized which has yet been investigated. Because of the novelty of the materials and the promising electrical characteristics as semiconductors or conductors, DOE support seems appropriate.

Presently we are completing the first phase of this work by establishing the interchain and intrachain exchange parameters, and developing a thorough understanding of the spin wave function symmetry and dynamics of the pure A and P. This may seem unnecessary in view of the concepts presented above, however it bears strongly on the correct description of these materials and is a subject of some controversy with regard to the existence of antiferromagnetic ordering and the presence of spin waves at low temperature. The compounds A, P, and $R(TCNQ)_x$ are Peierls semiconductors. Our future work, alluded to above, will proceed with greater insight and understanding if these pure compounds are properly understood.

The second area for which support is requested is the continuation of our study of hydrogen diffusion in bcc metals concentrating on the trapping of relatively low (<4 at.%) concentrations of hydrogen in V, Nb, and Ta and their alloys. Dr. R. S. Shalvoy (terminated 8/20/77) began this work using hydrogen in niobium

and established a body of experience extremely useful in carrying on further studies directed toward the role of trapping of H by interstitials. Our work in this area established our ability to prepare samples and to analyze the data in terms of the location of the hydrogen. Alloys containing no more than 4 at.% H pose problems of sensitivity but also leave us almost alone in the study of H in dilute solution. We now have the facilities and knowledge to upgrade Shalvoy's work considerably by extending it to the quantitative study of the trapping of hydrogen by interstitial elements such as boron, carbon, nitrogen and oxygen. Earlier work of this group (with E. von Meerwall) on oxygen and nitrogen in vanadium will be very useful in establishing the electronic structure and bonding nature of the trap site. A. B. Kunz has offered assistance in analyzing the trapping atom structure, and our experimental plan is to measure the resistivity as well as the magnetic resonance properties of these important ternary alloy systems, and the behavior of hydrogen in them. The relation between hydrogen diffusion and metallic embrittlement is well known.

Results FY78:

Most Significant Accomplishments: Our results on the organic charge transfer salts A and P, constitute the most significant accomplishment. The growth of large single crystals ($\sim 4\text{mm} \times 10\text{mm} \times 2\text{mm}$) of the salt A has provided the opportunity for resistivity and dielectric constant measurements as well as magnetic resonance and attempted Hall effect. In order to isolate the source of certain broadening effects, we have fully deuterated the methyltriphenylphosphonium molecule and shown that the salt P does not become antiferromagnetically ordered down to approximately 1.5 K, contrary to the conclusions of several other workers in the field. P undergoes a structural transformation at 45°C which we have not yet investigated. The salt A shows no such transformation. The importance of these results lies in the synthesis and characterization of organic crystals of a new and important class having electrical characteristics of probable importance to DOE. Furthermore, we are developing the techniques with which to investigate their novel electronic (and spin) properties including the charge density waves and their fluctuations.

Results Expected FY79: The longer range goal of the project as outlined under the above will be approached during this year with the controlled mutual substitution of the cation species in A, P, and R(TCNQ)_x. The electrical properties as a function of cation fraction and temperature will be carefully measured. Furthermore, manifestations of charge density wave (CDW) effects in the pure materials will be pursued vigorously.

The effect on the crystal structure of introducing foreign molecules is not yet known, however it can be surmised that the changes in the electrical properties will be worth investigating in any case. Consider two examples: Peierls nature of the crystal may be sufficiently disturbed (probably depending on cation solute concentration) that it disappears, giving rise to a different band structure, possibly metallic in nature. As an alternative, the substitution may alter the CDW pinning or may introduce strong aperiodic pinning into an otherwise unpinned or lightly pinned structure. We have devised experiments

to investigate these possibilities. Changes in the width or position of the band gap in these compounds brings us closer to an understanding of the meaning and the methods of producing the analog of n- and p-type crystals and junctions. Should the gap disappear, an effort to establish the reason for the metallic nature of the material will be made whether through simple identification or through chemical structural means. Our observational techniques are already well developed and, with the continued assistance of G. DePasquali with the chemistry, and others prepared to make physical measurements characterizing band structures, we are most optimistic about the value of this study to DOE in its materials program.

Although the work on hydrogen diffusion in niobium described in the above was not originally intended to be a study of hydrogen-interstitial interaction, it necessarily involved those impurities which were present in our samples. In view of the data analysis methods developed, and the knowledge in sample preparation gained, this work can now be conducted much more rapidly and with greatly improved experimental methods. These improvements will make it possible for us to survey a larger group of potential trapping species over an increased range of concentration. At high temperature the hydrogen can be expected to be free, but as the temperature is lowered the competition between the trapping sites and the hydride becomes of utmost importance. H. Wipf has suggested on the basis of his resistivity studies that thermodynamic equilibrium (in the way we understand its application in this particular case) is not achieved. We will check this for other solvent-trap pairs. The importance of avoiding hydride formation as the temperature of a containment vessel (for example) is lowered is clear. We believe we can go farther than an empirical statement of the hydrogen affinity of particular metal or alloy-trap pairs to a fundamental understanding of the phenomenon. This will require both relaxation time and quadrupole interaction measurements, both of which we are prepared to make, together with a theoretical analysis of the electronic structure of the trap.

Results Expected FY80: The scope of our investigation of the effects of cation substitution in the organic semiconductors A, P, and R(TCNQ) will be sufficiently broad that the ability to "tailor" the compounds will be within reason. Although we have not stressed the fact previously, an overriding consideration in determining their properties is their one-dimensional nature. This changes practically all of the electronic quantities with which we are so familiar in three dimensions, starting with the density of states. We can expect that appropriate anion substitution cannot only alter the one-dimensional electrical characteristics, but in addition provide limited control over the dimensionality of the structure. The limit will be fixed largely by our ability to find suitable cationic molecules for substitution into the A structure. Once these objectives have been achieved, we will concentrate on the earlier goal of investigating the properties of thin junctions of such crystals. Should these prove to be of no special interest, we will concentrate on the possibility of the metallic character which we expect to induce in some of these mixed salts, and explore the possibility of using the concepts developed to produce an electrically active (possibly conducting) polymer. Failing this, a solid state

reaction will be sought which might improve the chances for a useful junction diode. Throughout the investigation, we will be watchful for any variant of our crystals which exhibits high carrier mobility. Our analysis of the ideal material for a solar cell allows us to identify these organics as almost ideal, but lacking the requisite carrier mobility.

The structure of the bound pair (hydrogen-trapping atom) will be understood in sufficient detail that certain check experiments might be of use in determining whether the bound pairs exhibit any useful or unique properties which themselves could be exploited. The magnetic susceptibility as well as the superconducting properties should be investigated, and will be to the extent indicated by preliminary experiments during the course of the work. Opportunities to observe other trapping pairs will exist, and we will pursue these when appropriate and useful. It can be anticipated that one result of the proposed study will be hypotheses concerning the relative trapping ability of arbitrary pairs of interstitial atoms. Should the trap concept itself come under close scrutiny, it would be our intention to investigate more thoroughly the quantum electronic basis of the trap and the type of bonding that one can say is most closely approximated.

Relationship to Other Projects:

We have what could best be called an ongoing dialog with Chestnut, Soos, and others concerned with the structure of the organic materials mentioned in Item 16. In addition, the facilities and personnel of MRL are indispensable to this work. The advice and contributions of G. Stucky and G. DePasquali are responsible for the superiority of our samples and our confidence in reporting results.

Our contact with other groups and persons concerned with hydrogen in metals is much greater, in particular, with H. Birnbaum and coworkers in this Laboratory who have studied the motion of H in the vicinity of O and N by means of anelastic and strain relaxation techniques.

Publications (Calendar Year 1977):

T. J. Rowland and L. C. Labun
Effects of Crosslinking on Proton Spin-lattice Relaxation in Polybutadiene Macromolecules (accepted for publication)

T. J. Rowland and A. C. Yen
Field-Ion Microscope Observation of Copper and Copper--13 at% Beryllium Alloy Metallurgical Transactions (submitted to)

Theses (Calendar Year 1977):

None

Electron Paramagnetic Resonance Studies on Fast Ionic Conductors and on Catalytically Active Oxide Surfaces

Principal Investigator: Harvey J. Stapleton, Ph.D.
Professor of Physics

Supporting Agency: U. S. Department of Energy

Senior Staff: Harvey J. Stapleton, Professor

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Object: A) EPR on Fast Ionic Conductors. Because of their importance to energy technology, fast ionic conductors are currently under intensive investigation by experimentalists and theoreticians throughout the world. Among the fast ionic conductors, sodium beta alumina is the best conductor of Na^+ ions at moderate temperatures, and is useful as a sodium based battery electrolyte. One of the important remaining experimental problems (see for example J. C. Wang, J. Chem Phys. 65, 5378, Dec. 1976) is to determine the distribution of the Na^+ ions among the various possible sites in the conduction planes of sodium beta alumina. This research is aimed at such a determination in sodium beta alumina and in other beta aluminas containing silver, lithium or potassium ions.

We will accomplish this goal using techniques from electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR). Since such techniques require the presence of a paramagnetic species in the salt, we have chosen to minimize the perturbing influence of such a paramagnetic probe by converting non-magnetic O^{2-} ions, already present in the salt, to O^- through the technique of low temperature irradiation with electrons using the MRL Van de Graaf accelerator. We have identified a resulting magnetic center as an O^- ion in the ionic conduction plane, directly between two Al^{3+} ions.

O^- ions are missing a 2p electron in their outer shells and their magnetic properties can be described on the basis of a single 2p hole. Our EPR results to date strongly suggest that the 2p lobe of this hole lies in the ionic conduction plane. Through the use of ENDOR we expect to measure the hyperfine interaction between the 2p hole, situated at an oxygen site in the conduction plane, and the cations in the same plane. Each of these hyperfine (hf) interactions can then be broken down into two parts: (1) an isotropic contact interaction, and (2) a dipole-dipole interaction. It is a knowledge of this dipole-dipole contribution to the hf interaction which will allow us to determine the coordinates of the cations (Na^+ , Li^+ , K^+ , or Ag^+) relative to the oxygen site.

The data analysis implied here is by no means easy. There are many complications. One is that Na, Li, and K nuclei possess nuclear spins of 3/2, which means that quadrupolar splittings will also be present in the ENDOR spectrum. Silver, however, has a nuclear spin of 1/2 and thus will exhibit only hyperfine

interactions. Work on the silver salt should be no more difficult than the mapping of proton coordinates in lanthanum nicotinate dihydrate by Nd^{3+} --proton double resonance, which was published by C. A. Hutchison, Jr. and D. B. McKay (J. Chem. Phys. 66, 3311, 1977). The magnetic dipole interaction varies inversely as the cube of the separation between two point dipoles, i.e. as $1/R^3$, and a small correction is needed to compensate for the fact that one of the magnetic dipoles involved, the hole, is actually distributed over a p-orbital in O^- . These corrections have been published at least for special geometries (see for example O. F. Schirmer, J. Phys. Chem. Solids 29, 1407, 1968, W. P. Unruh, Y. Chen, and M. M. Abraham, Phys. Rev. B15, 4149, 1977) and computer programs exist (R. Bass, University of Kansas, private communication) for the general geometry. Such corrections to the separation inferred from the hf data generally work out to be less than 3%.

In summarizing the scope of our proposed work on fast ionic conductors, what we intend to measure is the distribution of the ionic carriers in the conduction plane of various beta aluminas through the analysis of ENDOR data which describe the hyperfine interaction between O^- ions and the conducting cations, Na^+ , Li^+ , K^+ , or Ag^+ , in the conduction plane. The O^- ions are produced by electron irradiation at 77 K and the EPR and ENDOR will be performed at microwave frequencies of 9.5 GHz and also at 15 GHz, if required. The samples will be examined at temperatures of 77 K and 1.5 K.

B) EPR on Surfaces of Catalytically Active Rare Earth Oxides. Rare earth oxides are effective catalysts in reactions involving the adsorption of hydrogen or oxygen. Yttria (Y_2O_3) and Lutetia (Lu_2O_3) preheated in hydrogen above 550 C are effective catalysts for the ortho-para conversion of hydrogen in which the active surface site is thought to be the paramagnetic Y^{2+} or Lu^{2+} ion. Terbium oxide catalyzes the oxidation of carbon monoxide to carbon dioxide. We propose to study the nature of the catalytically active sites in rare earth oxides using the powerful techniques of electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR). The latter technique can be applied to powdered samples in spite of the random orientation of the crystallite axes. If the EPR resonance spectrum is spread over a range of external magnetic field values, selective saturation at a particular magnetic field setting within the broad line can result in ENDOR signals associated with crystallites with an orientation resonant at the magnetic field setting. Conversely if the EPR line from the powder spectrum is narrow due to an approximately isotropic g-tensor, the ENDOR spectrum will exhibit strong responses at extremal values of the hyperfine and/or quadrupolar interactions because the number of crystallites contributing to the resonance will peak at extremal values.

It has been proposed by B. C. Gerstein of the Ames Laboratory (private communication) that the catalysis of CO oxidation by terbium takes place because the terbium ion on the surface of the oxide oscillates through two or more oxidation states. Tb_7O_{12} ($2\text{Tb}_2\text{O}_3 + 3\text{TbO}_2$) is apparently the catalytically active form. Tb^{3+} has an electronic configuration consisting of a xenon core plus $4f^8$. This even number of unpaired electrons (i.e., a non-Kramers ion) assures us that the spin-lattice relaxation time is extremely short and that no EPR resonance can

be seen except at liquid helium temperatures. Tb^{4+} , on the other hand, is isoelectronic with the S-state ion Gd^{3+} and might be expected to show an EPR signal even at room temperature corresponding to a g-value near 2.00. Even in a powder one of the seven transitions near $g = 2$ should persist if the analogy between Gd^{3+} and Tb^{4+} is valid.

We have examined the X-band EPR spectrum of Tb_2O_3 powders which have been exposed to O_2 at high temperature and found a large, broad (about 2 kG peak-to-peak derivative width) resonance line centered about a magnetic field value corresponding to $g = 4.1$. This suggests (see above) that the crystal field splitting of the Tb^{4+} ion on the surface of terbium is extremely strong in comparison to other S-state ions, i.e., producing splittings at least as large as 10 GHz. An examination of Gd_2O_3 powder revealed no anomalous behavior. We intend to probe the nature of the Tb^{4+} site in properly prepared Tb_7O_{12} by analysis of the EPR and ENDOR spectra of Tb^{4+} .

We also intend to apply EPR and ENDOR techniques to hydrogen-reduced Y_2O_3 and Lu_2O_3 powders to determine if the catalytically active site is really due to Y^{2+} and Lu^{2+} , as suggested in the literature. Because of the 7/2 nuclear spin of Lu, ENDOR data on that ion should provide us with information on the symmetry of the electric field gradients at the catalytically active surface site.

The structure of many rare earth oxides is a C-type cubic, known as the Bixbyite structure. The symmetry of the rare earth site in the bulk oxide crystal is quite complex. There are four inequivalent sites per unit cell having C_3 symmetry and six inequivalent sites of C_2 symmetry. Recently Y. Chen and¹ M. M. Abraham at ORNL have succeeded in developing a technique for growing single crystals of Y_2O_3 . It is anticipated that we will collaborate with them on some studies of rare earth ions in the bulk crystal to aid us in unraveling the spectrum of surface states on these same structures.

Results FY78:

Most Significant Accomplishments: Our EPR measurements on sodium beta alumina, irradiated at liquid nitrogen temperature with 1.5 MeV electrons, have led us to the following interpretation of the data. (1) O^- ions are the magnetic centers produced. (2) the p-orbital corresponding to the hole in the O^- electronic configuration lies in the conduction plane of the beta alumina. (3) The O^- center interacts with two equivalent Al^{3+} nuclei above and below the conduction plane. Result (3) is based upon the 11 line hyperfine (hf) pattern with a 1:2:3:4:5:6:5:4:3:2:1 intensity ratio indicative of 2 equivalent 5/2 nuclei. However, this clear hf pattern is badly washed out when the external magnetic field is in the conduction plane. This suggests that the various O^- centers are only equivalent when the external field is perpendicular to the conduction plane. In addition the measured g values suggest results (1) and (2).

These results are important because they establish the nature of the paramagnetic probe which we have introduced into the fast ionic conductor. With this knowledge of the O^- we can proceed toward our goal of measuring hf interactions with the

conducting ions and establish their distribution in space around the O^- center. One very surprising result is that the clearly defined 11 line Al hyperfine pattern is missing if the salt is irradiated with γ -rays at low temperature rather than with electrons. Experiments run at ORNL using their Co^{60} source reveal this fact.

Our EPR results on Tb_2O_3 heated in O_2 gas indicate that Tb^{4+} ($4f^7$, $^8S_{7/2}$), which is one of the important oxidation states of terbium oxide when used as a catalyst, gives an EPR spectrum very different from its isoelectronic neighbor Gd^{3+} . In a powder we expected to see at least one line (the $M_s = +1/2$ to $M_s = -1/2$ transition) at a g value of 2. Instead we found with our X-band (9.5 GHz) spectrometer a very broad (2 kG peak-to-peak derivative width) resonance corresponding to a g value of about 4.1. This suggests that the crystal field splitting of Tb^{4+} on the surface is large in comparison to the microwave quantum ($h\nu$ at 9.5 GHz). This is entirely different from Gd^{3+} ($4f^7$, $^8S_{7/2}$) in Gd_2O_3 powder which we also studied and found to give the expected results of a broad line at $g = 2$. A review of the literature reveals that Tb^{4+} has been investigated by EPR in a single crystal of ThO_2 (J. M. Baker, et al, Proc. Roy. Soc. A247, 141, 1958) and it exhibited a crystal field splitting comparable to an X-band microwave quantum. Such a crystal field splitting is about 15 times stronger for Tb^{4+} than for Gd^{3+} in the same host crystal, ThO_2 . Thus crystal field effects on Tb^{4+} in oxide catalysts are anomalously strong and may play an important role in the catalytic action of terbium oxide.

Other Results: In the four months since this research program was initiated we have converted an X-band spectrometer from one optimized for wide bandwidth (10 MHz), low power monitoring of transient spin effects at liquid helium temperature to one optimized for narrow bandwidth, high sensitivity at 77 K with rapid sample changing capability. This meant changing from a low power superheterodyne spectrometer with 18 Hz frequency modulation of the magnetic field to a high power crystal video detection system with 40 kHz field modulation and lock-in detection. Two TE_{011} wavemeter mode, liquid nitrogen cooled cavities were designed and built with vacuum insulation and a quartz tube for axial sample access and additional sample cooling with cold nitrogen gas. A high vacuum irradiation chamber was designed and built for the low temperature irradiation of the beta aluminas using the MRL Van de Graaff accelerator. A high vacuum system, made primarily of glass and quartz was designed and built to prepare the various rare earth oxide powders for our studies. O_2 , N_2 , and H_2 can be introduced at low flow rates over the powders while they are heated as high as 900 C. Theoretical calculations were also started during this period to compute the p-lobe corrections to the magnetic dipole-dipole interactions between the O^- ion and nearby ions with nuclear spins. Finally, a commercial B.E.T. surface area analyzer was purchased for general use by MRL personnel and it was necessary to check the instruments calibration against a more sophisticated instrument used for cement research on this campus, and to develop an operating manual for infrequent users of the equipment.

Results Expected FY79: During this period we intend to improve our understanding of the p-lobe orientations of the O^- center in the conduction plane of sodium

beta alumina, and to separate out of the $O^- - Al^{3+}$ hyperfine interaction that part which is due to dipolar interactions, and that part which is due to a Fermi contact interaction. When this is accomplished we will be able to calibrate our technique of using the dipole-dipole interaction to determine the position of cations near the O^- center, because the $Al^{3+} - O^-$ distance is known from the structure. At that point we will then proceed to a measurement of the distribution of mobile cation positions in the conduction plane using ENDOR data from the specific cation.

To accomplish this we will most likely have to design and construct an ENDOR system for use at 1.5 K to complement the ENDOR capability which was included in our newly modified spectrometer operating at 77 K. It will come as no surprise if ENDOR on these systems can only be observed at liquid helium temperatures. In addition we will learn the ion exchange techniques necessary to incorporate the various cations (Na^+ , K^+ , Li^+ , and Ag^+) in the beta alumina structure.

We also plan to study the catalytically active form of terbia (Tb_7O_{12}), specifically to obtain quantitative information on the extraordinarily large crystal field present at the Tb^{4+} sites. This will require EPR measurements at two temperatures (77 K and 1.5 K) and at two microwave frequencies (9.5 GHz and 15 GHz). We need to know if the crystal field splitting is of the order of 0.3 cm^{-1} or much, much larger than that. In the latter case, Fe^{3+} (the iron group analogue of Tb^{4+}) exhibits a totally isotropic g-value near 4.3 in various glasses where the perfectly rhombic symmetry fortuitously leads to a convergence of g_x , g_y , and g_z to a common value of 4.3. We have shown that a similar effect can happen for Tb^{4+} leading to a value near $g = 5$. Alternatively with splittings near 0.3 cm^{-1} , the broad low field resonance is due to several transitions which are not particularly sensitive to the magnetic field direction because the Zeeman perturbation is small compared to the crystal field effects at low magnetic field settings. EPR measurements at two temperature and two microwave frequencies will indicate which condition applies to Tb^{4+} .

We also expect to study the EPR and ENDOR spectrum of hydrogen-reduced Lu^{2+} in Lu_2O_3 to check the speculation that Lu^{2+} is the active center in that catalyst. We will also study the EPR spectrum of some rare earth ions in single crystals of Y_2O_3 , as they become available, in order to understand the complex symmetries of rare earth ions in their oxide state.

Results Expected FY80: During this period we expect to complete the data-taking phase of the ENDOR spectra of Ag^+ , Li^+ , K^+ , and Na^+ in the beta aluminas, and we will then enter the analysis phase. These spectra will contain, in general, the magnetic hyperfine interaction between O^- and the mobile cation, the interaction between the cation nuclear quadrupole moment and the electric field gradients at its position, and the cation nuclear Zeeman interaction. It is anticipated that substantial analysis on the MRL computer will be required to sort out the symmetries of the interactions and to arrive at the distribution of positions of the cations relative to the O^- site based on the dipole-dipole portion of the hyperfine interaction. Since Ag^+ has no nuclear quadrupole moment, its analysis should be the simplest, particularly since the contact hyperfine contribution is

probably negligible for most of the cations in beta alumina. We also expect to examine the EPR and ENDOR spectrum of hydrogen-reduced yttria for evidence that Y^{2+} is the catalytically active site in that material. In addition the use of O^{17} gas in the preparation of some of the rare earth oxides will be employed in order to introduce ligand hyperfine structure as a probe of the catalytically active site.

Relationship to Other Projects: Our research into the distribution of ionic carriers in the beta alumina is being conducted with strong interactions, consultation, and discussions with other investigators at this laboratory (primarily A. C. Anderson) and at Oak Ridge National Laboratory (M. Abraham, Y. Chen, J. Bates, and L. Jenkins). It is anticipated that we will require some collaboration with Professor R. Bass at the University of Kansas since he has efficient unpublished computer programs to calculate the p-orbital corrections to the $1/R^3$ dipole-dipole interaction when the dipoles are arbitrarily aligned relative to the p-lobe.

In the area of rare earth oxide catalysts we have benefitted from discussions with outside speakers at the catalysis seminars sponsored by the Ceramic Engineering Department. In particular, comments by B. C. Gerstein on catalysis by terbium were most helpful.

In connection with our work on yttria, we are collaborating with M. M. Abraham and Y. Chen at ORNL who have developed a technique for growing single crystals of Y_2O_3 . While their work is more concerned with bulk properties of Y_2O_3 as a high temperature ceramic material, they have sent us single crystal samples whose EPR spectrum will be helpful in understanding the EPR of surface states. I have an Oak Ridge Associated Universities contract which will cover travel expenses to ORNL to work there with Abraham and Chen on experiments of mutual interest.

Publications (Calendar Year 1977):

J. L. Boldu O., H. J. Stapleton, Y. Chen, and M. M. Abraham
Electron-Nuclear Double Resonance of V_{OD} Defects in SrO
Phys. Rev. B 16, 3875-3879 (1977)
Supported by ERDA under contract with Union Carbide (ORNL)

M. H. North and H. J. Stapleton
Electron Spin-Lattice Relaxation Rates of Octahedrally Coordinated
 Yb^{3+} in Cs_2NaYCl_6
J. Chem. Phys. 66, 4133-4140 (1977)
Supported by National Science Foundation Grant DMR-76-01058

Theses (Calendar Year 1977):

None

Oxide Catalysts

Principal Investigator: Gerald P. Wirtz, Ph.D.
Associate Professor of Ceramic Engineering

Supporting Agency: U. S. Department of Energy

Senior Staff: Gerald P. Wirtz, Associate Professor

Junior Staff: John J. Janecek, Research Assistant
David R. Kaar, Research Assistant

Object: The materials in this study are all of interest primarily for their potential significance in future energy applications. These oxides are seen both as candidates for certain applications in themselves and as archetypes of future materials to be engineered to specifications. Specific applications would include:

- 1) Solar collectors and heat mirrors.
- 2) Oxygen permeable conductors: (a) high temperature fuel cell electrodes, (b) separators for water electrolysis.
- 3) Interconnection materials for high temperature fuel cells, i.e., conductive materials connecting anode and cathode of successive cells in a fuel cell stack.
- 4) Oxidation catalysis.

While this list seems to encompass a diversity of applications, the common thread running through all is that the applications depend on transport properties in oxides which in turn are dependent on the defect structures of the oxides. These materials have ionic defect structures which are variable over wide ranges and electronic structures which translate these defects into variable electrical properties. While the application to oxidation catalysis may seem not to fit in this category, even here, surface defects certainly provide the active sites for catalysis. Furthermore, there is abundant evidence that the lattice oxygen participates in partial oxidation reactions over these materials. A basic premise of this research is that ionic transport within the lattice therefore is central to the catalytic process. The above list of applications is not intended to be exhaustive, but rather indicative of our interest in these materials. A complete list of potential applications would include thick film hybrid circuits, MHD electrodes, and transparent conductors for windscreen de-icers and electrooptic light valves of the PLZT type, among others.

The work would be characterized phenomenologically as the study of the relationship between defect structures and properties of oxides. The emphasis is on materials having very high concentrations of native point defects which often interact to form extended defects and impart unique properties to the material. For example, both Tl_2O_3 and $LaCoO_3$, under the proper conditions exhibit electronic conductivity characteristic of

a metal. Tl_2O_3 is a classical broad band degenerate semiconductor, while $LaCoO_3$ undergoes a semiconductor to metal transition at $\sim 937^\circ C$. Both materials are thought to have high oxygen mobilities at moderate temperatures, and $LaCoO_3$ has been studied extensively as a catalyst. As a catalyst, it is a model for the rare earth perovskites as a class of materials.

Thallic oxide is an archetypical non-transition metal oxide conductor. In_2O_3 and SnO_2 are other members of the class which have found extensive application as transparent electrodes for light valves and windscreen de-icers. These materials combine the properties of a wide gap and broad conduction band which makes them potentially transparent high mobility conductors. The carrier concentration is variable in the range of 10^{18} - 10^{21} cm^{-3} which enables the plasma edge to be controllably positioned in the near infrared-visible portion of the spectrum. At the same time, the high mobility should produce a sharp edge and good reflection in the infrared, properties required of a good heat mirror for flat plate solar collector applications.

DC electrical conductivity and Hall effect measurements between 4 and 300 K are made on single crystals to determine carrier sign, concentration, and mobility. Electronic scattering mechanisms are deduced from the temperature dependence of the Hall mobility. Electrical measurements are compared for crystals of different stoichiometry to determine defect and electronic structures. It can be shown that for a degenerate, non-transition metal sesquioxide semiconductor, $A = kT[\ln(n/2) + (\ln/2) Po_2 + 2\eta^*]$ where A is a constant of the material and η^* is the reduced Fermi energy $\eta^* = (E_F - E_C)/kT$. Assuming a density of states function in the conduction band, η^* can be calculated from the measured n . If the assumed density of states function is correct, then A will be a constant independent Po_2 . This has proven to be a very useful test for Tl_2O_3 crystals.

An extensive study of phase equilibria is ongoing for the La-Co-O system. The air isobar has been completely determined and equilibria off the air isobar determined in the vicinity of important compounds. Important portions of the liquidus surface and solidification paths remain to be determined. The primary motive behind the phase equilibria studies has been to acquire the information necessary to grow high quality single crystals of the mixed oxide phases for the determination of fundamental properties. At the same time the crystal growth studies are being pursued from the broader perspective that the growth of single crystal and polyphase oxide bodies from the melt will continue to increase in importance as a ceramic fabrication technique, particularly in energy related applications.

The use of galvanic cells utilizing CeO_2 and ZrO_2 based solid electrolytes to study thermodynamic and transport properties is of increasing importance to this work. Oxygen ion diffusion coefficients are most conveniently made using such a cell. A more novel measurement in such a cell is the adsorption of foreign material from the gas phase on oxide catalyst surfaces. The oxygen fugacity of the solid catalyst as sensed in such a cell is reduced in proportion to the degree of coverage of the surface by adsorbate. One can model curves of emf versus temperature assuming any of the standard isotherms and

adjust adsorption energies and partial pressures to match observed data. By quantitative coulometric titration it is hoped to measure the concentrations of active sites.

Results FY78:

Most Significant Accomplishments: With the analysis of the measurements on crystals annealed over a range of oxygen pressures, Tl_2O_3 has been thoroughly characterized as a highly degenerate semiconductor with a simple S-like conduction band. The donor states are doubly ionized oxygen vacancies in the lattice.

Other Results: The oxygen ion conductivity in Tl_2O_3 has been estimated to be of the order of $10^{-2} \Omega^{-1}\text{-cm}^{-1}$ at 650°C .

Expected Results FY79: We expect to be able to grow single crystals of $LaCoO_3$ from the melt by the end of FY79.

We hope to perfect the technique for making meaningful oxygen fugacity measurements during chemisorption on oxide catalysts.

Expected Results FY80: Electronic and ionic transport measurements on single crystal $LaCoO_3$ are expected to be underway. The semiconductor to metallic transition observed at 937°C in polycrystalline materials will be investigated.

Quantitative measurements of adsorption isotherms and their correlation with catalytic activity and active site concentrations of $LaCoO_3$ are expected to be made in this fiscal year.

Relationship to Other Projects: The research external to the University of Illinois to which this work is most closely related is research on high temperature fuel cells utilizing coal gas. It is secondarily related to MHD electrode research but this investigator has not been active in that field. The centers for work on high temperature fuel cells are Brookhaven National Laboratory and Westinghouse, in this country. Rare earth perovskite materials are the only real candidates for interconnector materials for this fuel cell with $LaCrO_3$ being the prime candidate. Other rare earth perovskites find application as oxygen electrodes. Brown, Boveri Company in Germany uses $LaNiO_3$ as the basic component of the cathode while Westinghouse is presently using a mixture of $PrCoO_3$ and In_2O_3 . The requirements of an interconnection material and a cathode are opposite with respect to oxygen ion transport. The search in cathode materials is for a material with an oxygen conductivity as high as the electrolyte, coupled with good electronic conductivity. Ionic transport in the interconnection would result in chemically short circuiting the cell. That both applications might be satisfied by such similar materials is surprising and points up the need for more basic research on this class of materials.

In the early models of high temperature fuel cells, In_2O_3 containing $\sim 10\%$ SnO_2 was the standard oxygen electrode. The present search is for an electronic conductor with higher oxygen mobility such that the current carrying capacity

of the cell is not dependent on the porosity of the electrode. Th_2O_3 is isostructural with In_2O_3 and measurements of equilibration rates on annealing in various oxygen pressures indicates that for "pure" Th_2O_3 crystals the oxygen conductivity is of the same order as the CeO_2 electrolyte. Considering the similarity of the In_2O_3 structure to the fluorite structure, a high oxygen mobility would be expected. The reason it is not observed in the electrodes fabricated is thought by this investigator to be due to the fact that the native oxygen vacancies are depleted from the structure in compensating for the tetravalent Sn^{4+} ion. Again, more fundamental research on transport properties and defect structures in these non-transition metal oxide conductors is needed.

An impressive amount of work, both experimental and theoretical, has been reported on the catalytic properties of LaCoO_3 . Interest was initially stimulated by the work of Meadowcroft, and Libby and coworkers. Some of the most detailed theoretical calculations on oxide catalysis have been made by Morin, Wolfram, and coworkers at North American Rockwell Science Center on perovskites, with emphasis on LaCoO_3 . The emphasis in the present work is on the preparation of materials (single crystals) on which fundamental property measurements are most meaningful.

At the University of Illinois, this work interfaces with the work of a sizeable number of investigators studying non-metallic catalysts. The work of W. S. Williams and A. B. Kunz and their students bears special mention.

Publications (Calendar Year):

V. N. Shukla and G. P. Wirtz

Electrical Conduction in Single Crystal Thallium Oxide: I. Crystals

"As Grown" from the Vapor in Air

J. Am. Ceram. Soc. 60, 253-258 (1977).

Supported by National Science Foundation DMR 76-01058

V. N. Shukla and G. P. Wirtz

Electrical Conduction in Single Crystal Thallium Oxide: II. Effects of

Annealing at 923 K in Oxygen Pressures from 0.01 to 1 Atmosphere

J. Am. Ceram. Soc. 60, 259-261 (1977)

Supported by National Science Foundation DMR 76-01058

J. J. Janecek and G. P. Wirtz

Ternary Compounds in the La-Co-O System

J. Am. Ceram. Soc. (accepted for publication)

M. S. Theses (Calendar Year 1977):

None

Ph.D. Theses (Calendar Year 1977):

Chyang John Yu (G. P. Wirtz, adviser)

Electrical Properties of Thallium Oxide Single Crystals Annealed in Oxygen

Also supported by National Science Foundation DMR 72-03026 and GH--3634

SUMMARY SOLID STATE PHYSICS

AK-01-02-02-2 Experimental Research

This program characterizes the atomic and electronic structure of materials of interest for energy systems. It is concerned with (1) Defects in Solids (2) Phase Transitions (3) Surfaces and Interfaces (4) Electronic Structures.

Defect research includes the effects of interstitial hydrogen and magnetic impurities on the properties of superconductors. Of primary interest is the useful development of superconducting properties through manipulation of electronic structure. The superconductivity of NbC_x will be investigated as a function of carbon content from this perspective.

Superionic conductors contain highly mobile cations with a poorly understood defect structure. Both RbAg_4I_5 and beta alumina will be investigated with emphasis on our recent evidence that the mobile cations in beta alumina can form an amorphous glass phase. We hope to confirm this novel model of the cation system.

As discussed earlier, the quantum properties of light elements like hydrogen in metals can dominate their behavior. In the solid helium phases, the quantum mechanical character of defects are uniquely available for investigation. We propose to measure the vacancy concentration in bcc ^3He - ^4He phases, examine defect-defect scattering in this quantum system, determine the characteristics of the delocalized quantum defects, and investigate the relationship of the vacancy concentration to premelting phenomena.

We will use our powerful ultrasonic techniques to characterize the structure of the hydrogen interstitial in niobium and determine the configuration of Al-Fe, Al-Mn and Al-Zn pairs in dilute aluminum alloys.

We intend to extend our studies of the relationship of dislocations to mechanical and thermal properties by investigating the mutual interactions of dislocations at the high dislocation densities of cold worked materials. To test the extrapolation of theory to complex disordered systems, the investigation will include polymer systems.

In the area of high temperature materials and defect properties, the investigation of anomalous diffusion in TiNb alloys will be completed and diffusion studies on zirconium initiated.

In parallel with the defect research we propose to investigate nonlinear elastic effects and lattice anharmonicity because of

their importance for thermal transport, thermal expansion, equations of state, and phase transitions. We anticipate a critical test of theory through determination of the equation of state of solid xenon and expect to use nonlinear elastic data to obtain equations of state for a variety of crystalline systems.

The investigation of phase transitions will include studies of solid methane to test current theories. An attempt will be made to obtain the order parameters associated with the transitions through an optical diffraction technique.

We will be investigating magnetic spin glass systems like Cu-Fe and Cu-Mn and plan to study by NMR techniques the phase transitions of these systems. We hope to determine the properties of the local magnetic field in the absence of an applied field--a critical experiment needed for comparison with theory.

A substantial effort will be concentrated on the properties of the transition metal dichalcogenide layer compounds like TaS₂, TaSe₂ and NbSe₂. The properties of charge density waves will be measured and from the temperature of the incommensurate to commensurate transition we expect to test McMillan's theory of "discommensurations".

The surface studies have two main thrusts. The first effort is focussed on the character of defect surface structures that are important for catalysis. The catalytic behavior of the tungsten, titanium and niobium carbides will be compared and a parallel theoretical investigation will attempt to interpret the results in terms of surface defect structure. A second effort is the electronic characterization of hydrocarbon catalysts that consist of small clusters of platinum atoms on oxide substrates. We hope to understand the properties of these systems which make them effective commercial catalysts in order to guide their future development.

Interface research is concentrated on thermal energy transfer across solid-solid and liquid-solid interfaces. We will measure the thermal boundary resistance between liquid helium and solids above 1 K where both experiment and theory contain ambiguities and the results are of practical value.

A knowledge of the electronic structure of crystals is fundamental to an understanding of their physical and chemical behavior. Some of the unresolved problems, like that of charge density waves, afford an opportunity to explore novel, sophisticated relationships which profoundly enlarge our understanding, although practical applications are not immediate. Other problems, as yet poorly understood, are obviously basic to the development of practical systems as in the examples of surface catalysis and solar energy semiconductor devices.

We will investigate both experimentally and theoretically the role of nitrogen in gallium arsenide-gallium phosphide mixed crystals. It is a sufficiently simple system to provide information on the role of deep traps in affecting the efficiencies of photovoltaic and luminescent devices.

We have shown that a combination of optical measurements and high pressure techniques is a powerful tool for characterizing the electronic structure of crystals and molecules of decisive importance for energy storage, energy transfer, luminescence and laser action. We propose new investigations of energy exchange in the halophosphates which are used for commercial fluorescent lighting and in the oxysulfides which are laser materials. We plan to characterize rare earth transition ion - organic chelates used for catalysis and chemical synthesis and examine the electronic structure of electron-donor complexes of which TTF-TCNQ is a well-known example.

The transition metal dichalcogenides are layered compounds with a surprising array of unusual properties---superconductivity, charge density waves, absorption of foreign molecules by intercalation between atomic planes. Their potential use as cathodes of efficient energy storage devices warrants investigation of their remarkable electronic properties. J. Dow will develop the theory of their low energy electron diffraction spectra and angular photoemission to permit the derivation of their electronic structure from experimental data. (A parallel program of F. Brown will be obtaining experimental data with support from NSF.) The theory will be extended to include the effects of alkali and rare gas intercalates. The experimental study of charge density waves in the layered dichalcogenides by C. P. Slichter with the theoretical cooperation of W. McMillan is an integral component of this collaborative research program.

AK-01-02-02-4 Particle-Solid Interactions

This activity is concerned primarily with the production of point defects, interstitial atoms and vacancies, by high energy electron irradiation of metals. The hexagonal metals Mg, Zn, Cd, and the bcc metals Nb and V are under study. Annealing studies after irradiation are used to identify and characterize the radiation induced defects. Despite intensive investigation of the fcc metals, the response of the bcc and hexagonal metals to radiation is inadequately understood and the apparent possibility of long range interstitial migration at temperatures below 2 K poses significant problems within the framework of general defect studies.

AK-01-02-02-2 Experimental ResearchLow Temperature Studies of Defects in Solids

Principal Investigator: Ansel C. Anderson, Ph.D.
Professor of Physics

Supporting Agency: U. S. Department of Energy

Senior Staff: Ansel C. Anderson, Professor
Mark Steinback, Research Associate

Junior Staff: Philip J. Anthony, Research Assistant
James A. Katerberg, Research Assistant
Emanuel P. Roth, Research Assistant
Terry L. Smith, Research Assistant and Fellow

Object: The purpose of this project is to obtain experimental data on a variety of defect structures in solids, both (i) to provide a basic understanding of the defect and (ii) to permit a prediction of the behavior of bulk properties when defects are present. Reduced temperatures (0.02-300 K) are used in the investigation since such data are often more amenable to theoretical interpretation and thus provide a foundation for a general theoretical development, and because some important phenomena, such as superconductivity, occur only at low temperatures. Several measurement techniques are used, including thermal and electrical conductivity, specific heat, thermal expansion, ultrasonics and dielectric polarization. As an example, low temperature thermal conductivity measurements provide both technical data, appropriate to engineering cryogenic phenomena, and a source of very high frequency phonons to probe the dynamic response of defect structures.

Four generalized classes of defects are discussed below. It is emphasized that our primary objective is to gain a basic understanding of the defects and their behavior. But each material and/or defect is also relevant to an energy-related problem. This relationship is discussed briefly. We wish also to stress the cohesiveness of the program. Progress in one area of investigation has been, and continues to be, closely related to parallel progress in a separate area.

1. Dislocations and Grain Boundaries. These extended defects not only dictate the strength of many materials, but also limit the thermal conductivity of superconductors and crystalline dielectrics at reduced temperatures. Therefore they influence, for example, the thermal stability of superconducting composites, which are discussed below.

The measured cross section for the scattering of a lattice wave or phonon by a dislocation has been widely reported to be a factor of 10^3 larger than predicted by theory, while scattering from grain boundaries has been reported to be a factor of 10^4 larger than predicted. We have shown that the factor of 10^3 discrepancy between theory and experiment is caused by localized motion of the

dislocation which occurs even at very low temperatures. This motion is influenced by the lattice potential and by impurities. The factor of 10^4 discrepancy for grain boundaries resulted from poor experimental procedure; here experiment and theory are consistent.

Our measurements thus far have included only a low density of noninteracting edge dislocations or low-angle grain boundaries. We are not interested in investigating the more practical problem of cold-worked materials having a high dislocation density caused by compression or torsion. Here the interaction between dislocations becomes important. We will continue to use thermal conductivity and ballistic phonon measurements. Gamma-irradiation will be utilized to partially or fully immobilize the dislocations.

2. Interfaces and Surfaces. We are mainly interested in the transfer of thermal energy across surfaces, which include both grain boundaries and interfaces between different materials (generally called the thermal boundary resistance). Heat transfer along and across superconductor-insulator interfaces is a determinant in the efficiency and thermal stability of superconducting windings used in generators and motors and in future energy storage and magnetohydrodynamic energy conversion techniques. Catastrophic failures due to quench must be prevented without the requirement of excessively conservative design. Heat transfer to a liquid or gaseous cryogen affects the efficiency and stability of superconducting electrical power transmission cables. Very little experimental information is available as yet, especially in the presence of insulation (polymers) and neutron or other radiation. In the area of catalysis, it has been suggested by others that the thermal boundary resistance effects both the activity and stability of catalytic particles dispersed on a substrate.

We have made contributions both to the engineering lore and to the theoretical understanding of the thermal boundary resistance between solid materials. The transfer of thermal energy between two solids is now well understood. The major remaining unsolved problem is the thermal boundary resistance to cryogenic liquid or gaseous ^3He or ^4He , or to solid ^3He , ^4He , H_2 or D_2 at "practical" temperatures above 1 K where the original theory is in error by a factor of 10-100. More recent theories give the appropriate magnitude, but contain adjustable parameters not available experimentally. On the other hand, experiments give different quantitative results depending on the measuring technique. We therefore plan to use two techniques simultaneously in an effort to understand the experimental problem. This will also provide a clue to the failure of theory.

3. Disorder in Superionic and Solid Ionic Conductors. These are important in fast ion transport devices, such as batteries of high energy density. The highly mobile ions of most superionic conductors undergo ordering at reduced temperatures. The conducting ions in crystalline β -alumina, however, appear to undergo a "glass" transition. That is the specific heat and thermal conductivity have behavior which is common to nearly all amorphous materials. We will therefore measure other properties (thermal expansion, dielectric constant) to

determine if, indeed, the cations behave as if arranged in a glass. This will eventually provide information on cation structure or arrangement not available, for example, from x-ray examination, and should also provide valuable insight into the behavior of actual glasses which are not yet understood.

The solid ionic conductor Li_3N will be subjected to the same experimental measurements used on the β -aluminas. The Li_3N is a material which may also be of use in the blankets of deuterium-tritium fusion reactors.

4. Hydrogen Effects in Metals. The strength of some metals and alloys is affected by hydrogen embrittlement, which is partly caused by relatively fast hydrogen diffusion. We have shown that interstitial H (or D) moves rapidly in Nb, V, and Ta, even at extremely low temperatures, by quantum mechanical tunneling. This demonstrates the highly delocalized nature of the interstitial H (or D). It was also noted that dislocations produced by β -phase precipitation of H can reduce the thermal conductivity of superconductors. More recently both the theoretical and the experimental efforts have been taken up by other groups. We do wish however to study the possibility of H and D tunneling in the rare-earth metals such as Lu, and to observe the effect of H or D on the thermal expansion of metals. This will further check the current ideas of H motion. It will also provide a model for looking at localized excitations and defects (such as dislocations) in other systems using thermal expansion measurements.

As H (or D) is added to Pd, the metal becomes a superconductor for reasons not yet clear. We will measure the effect of H(D) concentration on the superconducting transition temperature over a much wider temperature range than previously attempted. The data should provide a test of the several theories which have been proposed, and help clarify the role of the nonstoichiometric H or D.

5. Cryogenic Instrumentation. Much of the instrumentation needed in the project is not available commercially, and so a part of our effort is devoted to development of new or improved technology. Two subprojects are currently underway.

Low Temperature Thermometry. Temperature measurements are essential to any research on the properties of materials at reduced temperatures. The most convenient and widely used technique (≤ 10 K) has been resistance thermometry in which tiny chips of carbon or germanium are utilized as the thermometric material. The resistance measurement must not, however, heat the thermometer above its environment. Hence very sensitive bridges must be used.

Above ≈ 0.5 K Ge resistance thermometers have proven to be very stable. We are extending the use of Ge thermometers to below 0.02 K. The effort has been underway for five years, and includes: a) cooperation with manufacturers to provide designs appropriated to the range ≤ 0.5 K, b) development of a 4-terminal ac bridge of optimum signal/noise to measure resistance, c) assembling vapor pressure, magnetic noise, and superconducting fixed-point thermometers to calibrate the Ge (commercial calibration below 0.5 K has been highly unreliable), and d) our current determinations of thermal impedances within different

Ge units, so that the design of the unit and the measuring power used may be optimized.

Since Ge thermometers are so easily overheated by spurious radio frequency and other currents, we are developing a superconducting Be "fixed-point" device which can check the operation of Ge thermometers near 0.024 K. The problem is to null all magnetic fields and suppress supercooling of the Be superconducting transition, yet have a small package for use in an experimental cryostat.

Thermal Expansion Apparatus. A knowledge of thermal expansion coefficients are very important to cryogenic engineering. But they also provide information about excitations and defects within a material. Thermal expansion coefficients at low temperatures are generally very small, so the measuring apparatus must have high resolution. We have obtained a resolution of 0.01 Å and should be able to improve this by a factor of 10 or possibly 100. The completed dilatometer would be used in research discussed under 1, 3, and 4 above.

Results FY78:

Most Significant Accomplishments: Our most significant advance has been in the area of thermal boundary resistance. There were three accomplishments:

- 1) We have shown that several new theories purporting to improve or correct the original "acoustic-mismatch" theory are actually identical with the older theory. The crux lies in understanding what thermometers actually measure under nonequilibrium conditions such as found in thermal transport. As a result of our work (i) the theory is on a more firm foundation than previously and (ii) the role of the thermometer in thermal transport measurements has been elucidated.
- 2) For two solids in contact, the only major deviation between theory and experiment has occurred when one solid was a polymer. We have shown that the deviation is caused by the strong frequency dependent phonon thermal transport in the polymer, which is similar to that of other amorphous materials. Hence, the theory of boundary resistance is, itself, correct but must in some cases be applied in a more subtle fashion than realized previously.
- 3) The one case where the theory does fail is for the interface with liquid or gaseous ^3He or ^4He , or solid ^3He ^4He , H_2 and D_2 at temperatures above roughly 1 K. The measured thermal resistance is a factor of 10-100 smaller than predicted by theory. We have obtained quantitative measurements of the boundary resistance for ^4He , H_2 , D_2 and Ne in contact with the same Cu surface. The deviation between theory and experiment is shown to scale with the extent of quantum behavior of the liquified or solidified gas. The theoretical significance of this is not understood as yet. The data have, however, served to eliminate several theoretical models proposed to explain the factor of 10-100 anomaly.

The practical importance of the thermal boundary resistance has been discussed under Item 16(2).

Other Results: 1) It has been shown that the cations, in the crystalline superionic conductor β -alumina, have certain properties characteristic of a glassy material. The extent of the glass-like behavior depends on the cation present in the crystal (i.e., Na, Li, Ag, etc.). If this conclusion is supported by ongoing measurements of yet other physical properties, there will be two important consequences. First, we will have information on the ground state behavior and extent of delocalization of the highly mobile cations, and of the importance of quantum effects. Second, the β -alumina system should provide an ideal test for theories of the behavior of actual glasses and polymers, and in particular it should provide an indication as to the physical description of the localized excitations found in all amorphous materials.

2) We have shown that the scattering of phonons by low-angle grain boundaries is compatible with existing theory. The factor of 10^4 difference reported in the literature is spurious.

3) The low temperature specific heats, thermal conductivities and ultrasonic velocities of two polymers (epoxies) may be explained by the tunneling-states model of amorphous materials. Also, variation of the cross-link density modifies only the density of localized excitations. This behavior is identical to that found in fused silica when the density of localized excitations is modified by neutron irradiation. Our results further confirm the universal behavior found in different disordered materials.

4) The thermal resistance of glassy carbons is dominated by the presence of microvoids rather than the localized excitations of amorphous materials. Hence, as in partially crystallized ceramics, the thermal conductivity could be tailored during manufacture.

5) The primary impediment to the removal of measuring power from Ge resistance thermometers at very low temperatures is a weak carrier-phonon interaction. Thus, efforts to improve thermal contact to these thermometers will be futile unless this intrinsic coupling can be enhanced.

Results Expected FY79:

1) We expect to complete the work on the superionic conductors β -alumina and Li_3N , and their possible relationship to glassy materials; a relationship which could be of value in understanding both the superionic conductors and glasses.

2) We will complete a study of localized dislocation motion at high dislocation densities. This will indicate the importance of dislocation-dislocation interaction, and should clarify some problems between theory and experiment found in the literature and currently under study theoretically.

3) We will attempt to measure the thermal boundary resistance between liquid He and several materials, primarily at temperatures above 1 K, using two different measurement techniques simultaneously. This work should help determine why different techniques give different results.

4) Our study of the relationship between H or D content and the superconducting transition temperature of Pd should be complete. The results will provide a test of the several theories proposed to account for the transition.

5) We plan to investigate the defects produced in crystalline quartz through neutron irradiation using thermal conductivity, ballistic phonon, specific heat, ultrasonic velocity and dielectric susceptibility measurements over a broad range of temperatures (0.03 - 300 K) and defect concentration. At the higher defect concentrations, there should be an important correlation with the localized excitations we have studied in fused quartz.

6) We will continue to measure the properties of additional engineering materials, such as specialized polymers, at reduced temperatures. This will provide engineering data, but will also determine if theory developed from work on simple materials may be extrapolated to more complex systems.

7) In the area of cryogenic technology, we should finish the thermal expansion apparatus for use in studying the several defect systems discussed above. Also, we hope the Be superconducting "fixed-point" thermometer can be built and thoroughly tested.

Results Expected FY80:

1) The measurements of thermal boundary resistance between liquid He and several materials, both metallic and dielectric, should be completed.

2) The study of neutron-produced defects in crystalline quartz will be continued. The more heavily irradiated samples must be measured last because of self-heating from radioactive decay. Hence, the measurements will extend over a long period of time. We believe it is important to work with samples cut from the same crystal to be certain that differences in measured properties are related to the irradiation.

3) We plan to measure the thermal expansion associated with several defect systems and of materials of technical interest.

Relationship to Other Projects: All electrical supports and insulation for cryogenic equipment (power generation, storage, and transmission, motors and generators, Josephson junction technology) will utilize polymers and ceramics. Yet little is known about these materials at reduced temperatures. Additional knowledge would permit the development of better engineering materials to minimize, for example, the refrigeration power required. Most of our effort concerning the basic physics of glassy materials is carried out under NSF contract DMR-77-08599. It includes work on glasses, polymers (including rubber), and glassy metals, and the effects of radiation damage, thermal history, etc. We have obtained considerable information concerning the localized excitations associated with disorder. This research is mentioned here because a) facilities developed under the present contract have been used; and b) the results of the NSF project are very important to the work discussed in the present report. We

have, for example, explained the thermal conductivity behavior of partly crystallized ceramics, porous materials, and the recently developed glassy carbons. In brief, the work supported by ERDA has been directed primarily to those disordered materials and systems having more practical significance to energy related applications.

Within my laboratory we have developed an excellent facility for obtaining measurements in a temperature range four decades wide, 0.02 - 300 K. Because of the variety of materials investigated, it is not feasible to prepare all samples used. Thus our closest and most important cooperation is with groups having the necessary equipment and experience to prepare and/or characterize specialized materials. In this respect we collaborate with H. K. Birnbaum (MRL) on H or D in Nb, V and Ta, with T. J. Rowland (MRL) and D. S. Pearson (Northwestern University) on polybutadiene, with C. B. Satterthwaite (Physics) on H or D in Pd, and possibly with K. A. Gschneidner (Ames Laboratory - ERDA) on H or D in Lu. There is also collaboration with laboratories at Corning Glass Works on glasses, Allied Chemical on glassy metals, 3M on polymers, Exxon on superionic conductors, Lake Shore Cryotronics and Cryocal on Ge thermometers, the Argonne National Laboratory on β -alumina, and the National Bureau of Standards on thermal boundary resistance and superconducting fixed-point devices.

The interaction at the theoretical level with several individuals in MRL or the Physics Department at the University of Illinois should also be emphasized. This includes J. D. Dow, C. P. Flynn, A. V. Granato, J. S. Koehler, E. A. Jackson, and W. L. McMillan.

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J. R. Matey and A. C. Anderson

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Supported by National Science Foundation Grants DMR-75-09566 and

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T. L. Smith, P. Anthony, and A. C. Anderson

Density of Low Energy Excitations in Neutron Irradiated Vitreous Silica

Phys. Rev. (submitted to)

Also supported by National Science Foundation DMR-77-08599

Theses (Calendar Year 1977):

None

Response of Solids to Electromagnetic Radiation

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Object: The main theme of this research is a study of the response of various materials to excitation by light and by electrons; our interests focus on four main areas: (i) attempts to understand the low energy electron diffraction (LEED) spectra of transition metal dichalcogenides, (ii) studies of the role of electronic relaxation in determining the synchrotron radiation spectra of metals, (iii) studies of the effects of rare gas and alkali adsorbates and of alkali intercalates on LEED spectra of transition metal dichalcogenides, (iv) the theory of angular distributions of photoelectrons emitted from layered solids.

Our studies of the LEED spectra of transition metal dichalcogenides have centered on TiSe_2 , which is unique in that it exhibits a charge density wave phase in the bulk but not in the surface-sensitive LEED experiment. We hope to elucidate the mechanism by which the charge density wave is quenched at the surface and to understand its dependences on distance from the surface, adsorbates, and intercalates. Analysis of LEED data for pure TiSe_2 suggests that an outward relaxation of the surface occurs, possibly altering the surface band structure of this semi-metal enough to prevent formation of the charge density wave. Parallel studies of photoemission angular distributions should give information about the depth dependence of the charge density waves, because photoemission excited with different soft x-ray wavelength samples different electron escape depths.

Studies of electronic relaxation effects in synchrotron radiation excited metals have focused primarily on the anomalous lineshapes observed at x-ray absorption and photoemission edges in simple metals, and on absorption lineshapes of rare gas impurities in alkali hosts. Multi-electron Coulomb and exchange interactions can have pronounced effects on the observed lineshapes and line positions, and a complete quantitative understanding of these very fundamental effects is currently in an early stage of evolution. We have concentrated on using general arguments, sum rules, and simple models in order to understand the essential physical consequences of the complicated many-body interactions.

There are a number of practical aspects of our work highly relevant to DOE's energy mission. Transition metal dichalcogenides appear to have great promise

as cathodes for high energy density 2.4 V batteries. One promising mechanism for electrical storage involves TiS_2 cathodes, Li anodes, and $\text{Li}^+ \text{ClO}_4^-$ (all light, inexpensive and available elements). The electrical storage is believed to proceed through an intercalation reaction. We shall be trying to understand the nature of intercalation in these materials and the effects of intercalates on charge density waves and vice versa.

Our extensive theoretical studies of materials excited by synchrotron radiation have been designed to determine the importance of multi-electron relaxation in these spectra and to develop simple methods for computing such relaxation effects for real metals. Although our research has been basic, the spectral lineshapes which we calculate appear to be promising "tags" for characterizing impurities in metals, for studying chemical reactions occurring at metal surfaces, and for studying metal-semiconductor interfaces.

The efficiencies of photovoltaic and electroluminescent devices are limited by trap levels deep within the forbidden band gap; our recently completed study of the nitrogen isoelectronic trap in $\text{GaAs}_{1-x}\text{P}_x$ identified this system as a prototype of a trap which is shallow in a binary crystal (GaP) but becomes deep in the alloy. As such, it represents one of the simplest systems for studying and better understanding how the lattice deformations around an impurity affect its properties as a deep trap.

Our calculations of two-photon absorption spectra of semiconductors in intense electric fields should stimulate more experiments on the nonlinear optics of semiconductors and insulators in intense fields. The next generation of electronic and electrooptic devices will likely be limited by the breakdown electric fields which occur at high doping levels, and some optical lenses will suffer field-breakdown induced by the electric fields of high-intensity laser light.

Results FY78:

Most Significant Accomplishments: A simplified method of computing transition-metal-dichalcogenide low energy electron diffraction spectra has been developed, which greatly facilitates the determination of surface relaxation. With this method, one solves the multiple-scattering problem for two atomic layers, treats interlayer scattering in a single reflection approximation, and then relaxes the atomic positions until the theory reproduces the principal observed LEED peaks. The method is sufficiently reliable that only one full-multiple-scattering LEED calculation is necessary, and therefore eliminates the costly iterative multiple-scattering computational schemes presently in use, while at the same time offering a simple prescription for identifying LEED peaks without performing a lengthy calculation. With the method we have determined that the outermost layer of TiSe_2 most probably relaxes outward slightly, an effect which may prevent formation of the charge density wave phase at the surface.

Other Results: The two-photon electroabsorption lineshape for a semiconductor in an intense electric field has been computed. This is, we believe, the

first theory of the non-linear optical response of excitons in the electric field-ionization limit.

The x-ray photoemission lineshapes of core levels in free-electron metals have been computed using a simplified multi-electron relaxation model. By means of exact model calculations we have shown that the lineshape depends on the form of the electron-hole interaction, that existing interpretations of photoemission data which neglect this form may be imprecise, and that therefore an entire body of previously conflicting x-ray experiments can be given a unified explanation.

Measurements of angular distributions of photoelectrons ejected from rare gas atoms have been analyzed, yielding empirical pseudopotentials and cross sections valid for photoelectron energies of 100 eV and greater. These pseudopotentials will be employed in analyses of LEED data.

Results Expected FY79: We expect to complete our calculations of the low energy electron diffraction spectra for all the transition metal dichalcogenides, including surface relaxation, following the lines developed for TiSe_2 . We then plan to extend the calculational scheme to compute photoemission angular distributions and band structure, in an effort to predict from a single theory the optical, x-ray, and low-energy electron response of these materials.

Following this, we shall develop techniques for studying the changes in these spectra induced by alkali and rare gas intercalates and adsorbates. The present layer-by-layer computational scheme has been developed expressly for this purpose. With these calculations and the data of Professor Brown's group, we hope to understand if and how charge density waves are pinned by surface impurities and intercalates, which sites intercalates and adsorbates occupy, and how impurities cause the lattice to relax.

An attempt will be made to formulate the problem of photoabsorption by impurities in metals along lines similar to those employed for soft x-ray absorption in pure metals. The introduction of an extra orbital in the impurity problem seems to offer a mechanism for production of the presently-mysterious observed nearly-linear absorption threshold shape (as a function of energy).

Results Expected FY80: The calculations of synchrotron radiation absorption and photoemission spectra will turn to studies of transition metals, where the electron-hole interactions are strong (unlike the alkali and noble metals) and where the spectra are more complicated. The extension of our theory of rare gas impurities in alkali hosts will be dictated by the success of the initial theory and by available data. If the theory appears tractable, we shall begin investigating electronic relaxation effects at metal-semiconductor and metal-vacuum interfaces.

The LEED and photoemission program will proceed to study more complicated adsorbates and intercalates, as dictated by the experimental data available

and by our desire to better understand the interactions of charge density waves with their host material.

Relationship to Other Projects: This theoretical project is meant to cooperate with and assist various experimental programs at the University of Illinois. The studies on $\text{GaAs}_{1-x}\text{P}_x\text{:N}$ have resulted in joint publications with the experimental groups of Professors Streetman and Holonyak of the Electrical Engineering Department; the LEED studies are designed to assist Professor F. Brown's experimental program, and provide data analyses not otherwise available locally; some of the synchrotron radiation studies have been in collaboration with Professor C. P. Flynn. The MRL program is complementary to NSF funded research, which, for example, is computing Kohn Sham atomic potentials for x-ray excitations of rare gases--we plan to employ these pseudopotentials in LEED studies of rare gas overlayers on transition metal dichalcogenides.

Our results on synchrotron radiation spectroscopy have stimulated the Northwestern theory group to reinvestigate the band theory of simple metals, and to demonstrate that the response to synchrotron radiation of even the simple metals Na and Mg is nonfree electron like. At the present we are engaged in collaborative research with groups at Northwestern, Caltech, North Carolina, Princeton, and Argonne.

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Theses (Calendar Year 1977):

None

Use of Very High Pressure to Investigate the Structure of Matter

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Object: The fundamental thesis of our research program is that very high pressure is a most powerful, indeed an essential, variable for understanding electronic structure and electronic behavior in condensed systems. The central feature of this research has been the selection of those classes of materials and types of measurements which yield the most important information and most useful generalization about electronic phenomena. Incidental to this process has been the development of techniques for measuring various features of optical absorption and emission spectra and of Mössbauer resonance spectra as well as electrical resistance to relatively high pressures, in some cases to several hundred kilobars.

The basic effect of pressure is to decrease interatomic distance and thus to increase the overlap between adjacent electronic orbitals. As a consequence, the energy of any one electronic state, in general, changes with respect to that of other states. The information which can be extracted from these energy shifts can conveniently be classified in three categories.

- (a) It is possible to characterize electronic energy states and excitations.
- (b) It is possible to perform critical tests of theories and hypotheses concerning electronic processes.
- (c) In a wide variety of materials the relative shift in energy is sufficient to establish a new ground state for the system (or to modify its characteristics greatly by configuration interaction). These new ground states may have new and interesting physical and chemical properties. Studies of pressure-induced

electronic transitions have contributed considerably to our understanding of electronic phenomena.

Currently our research centers around high pressure luminescence and photochemistry. We are finding it to be the most flexible and most fruitful of all the techniques we have used in our high pressure studies over the past 30 years. In addition to information on peak energy and shape as a function of pressure, one can measure intensities (luminescence efficiency) and lifetimes. One can study allowed transitions (fluorescence) or forbidden transitions (phosphorescence). We have modified our high pressure apparatus to permit measurements in solids and polymers to 150 kilobars over a temperature range 77-450 K, and in liquids to 12 kilobars over a moderate temperature range. With the availability of modern electronics (photon counting equipment) and fast flash lamps and lasers, we can measure spectra over the range 250-2000 nanometers, quantum efficiencies as low as 10^{-6} and lifetimes as short as a few nanoseconds.

As discussed in Sections 18-20, we are applying these techniques to the study of luminescence efficiency, radiationless transition rates, spin-orbit coupling, energy transfer and photoconductivity in a wide variety of materials. These range from crystalline inorganic solids such as alkali halides, zinc sulfide and calcium molybdate through metallorganic crystals, crystalline organic materials, and molecules suspended in various plastic media, to ions and molecules in a variety of liquid solvents. The common thread in the research is that with pressure we perturb the energy levels of the entity under study and the nature of the interaction with the environment. The pressure induced perturbations can be more clearly and unambiguously described and are frequently larger in magnitude than those introduced by changing temperature or composition. We can thus extract a better characterization of electronic states and a more clear cut test of theories. These results lead in time to better design of useful materials.

Applications. While the thrust of our studies is basic, it seems useful to mention a number of areas in which the results could reasonably find application.

1) Our pressure experiments involve the effect of pressure on the interaction of light with solids, liquids and polymers. Direct tests are made of theories of radiant energy absorption and emission, of energy transfer, energy storage and the transformation of optical energy into electrical, chemical or thermal energy. In particular, we feel that a better understanding of high pressure organic photochemistry and photoelectronic transport in solutions and polymers could open up new methods of solar energy conversion, and help develop new materials for this conversion process.

2) Another obvious area is in understanding of the efficiency of phosphors and ultimately in the design of better phosphors with less energy consumption per unit of output. Fluorescent lighting is a significant consumer of electrical energy.

3) The understanding of energy transfer is essential in fluorescent lighting, in the activation of lasers, and in photochemical processes such as photosynthesis.

4) Luminescence efficiency in liquids is frequently strongly dependent on solvent properties. With pressure one can separate effects of temperature, of composition, of polarizability and of viscosity. One can establish the mechanism of many photochemical processes and the nature of the controlling variables. Where the efficiency is strongly viscosity dependent, one can use the luminescence output as a measure of viscosity in locations such as at the surface of bearings, where conventional methods are inapplicable.

Results FY78:

Most Significant Accomplishments: 1) We have made comprehensive studies of fluorescence efficiency as a function of pressure for both organic and inorganic systems where the limiting process in the efficiency is a direct radiationless transfer to the ground state (internal conversion). For a series of azulene derivatives in several polymers, we have demonstrated the direct relationship between the energy of the emission and the fluorescence efficiency. Azulene derivatives are very unusual in that emission is observed from two excited states with quite different electronic configurations. The change of peak energy and the change in emission efficiency with pressure were quite different for the different states and, for a given state, for various polymeric media with different polarizabilities. This is a unique example of the effect of interaction of electronic configurations on luminescence efficiency.

In a study of a series of crystalline tungstate and molybdate phosphors we were able to demonstrate that one can quantitatively predict changes in fluorescence efficiency and lifetime with pressure and temperature from the measured changes in emission peak location and peak shape with pressure (and temperature). This is the first comprehensive quantitative test of the use of the quantum mechanical configuration coordinate model for this purpose and puts the predictions of this model on a much firmer basis.

2) We have made a detached comprehensive study of the effects of pressure on the optical absorption and emission properties of a series of anils and related compounds. These materials can undergo a change of configuration (cis-trans isomerization) and/or a hydrogen transfer (keto-enol) under the action of light (photochromism) or heat (thermochromism). These changes introduce a new absorption peak in the visible part of the spectrum and a dramatic change of color. The compounds are of interest as possible energy storage materials, as potential electronic switches and as models for rhodopsin--the chemical responsible for vision.

At one atmosphere, the crystalline anils are either photochromic or thermochromic but the processes are mutually exclusive. In polymer films all anils are photochromic, but thermochromism is never observed. We have been able

to show that at sufficiently high pressure one can induce the thermal transition at room temperature in either the photochromic or thermochromic crystals, and, under some circumstances, in the polymer films. Pressure also has dramatic effect on the rate of the photochromic process in crystals and in polymers.

From our studies of the effect of pressure and temperature on yields, rates, and luminescence efficiency, we have been able to sort out the various steps in the processes involved, e.g., which take place between metastable ground states and which between optically excited states, and what kinds of thermal barriers are involved in the various steps. These results conclusively answer a number of questions which have long persisted concerning these much studied and potentially useful compounds.

3) The luminescence efficiency of many phosphors depends strongly on the nature of the solvent. A number of dyes such as crystal violet (CV) are largely quenched in nonviscous fluids but fluoresce strongly in liquids like glycerol. The standard methods of studying the effect of viscosity are by varying the temperature or the composition. The problem is that either of these methods introduce parameters other than the viscosity. With pressure we can vary the viscosity of fluids by as much as three orders of magnitude at constant temperature. Using this technique, we have performed the first thorough test of the theory of Förster and Hoffman which is widely used for this situation. We find it fits quite well at intermediate and high viscosities but is clearly inadequate in the low viscosity range. The theory is important in understanding scintillation counters and solution photochemistry.

This work is the initial stage of an extensive program for studying the effects of viscosity on optical properties. Some other aspects are mentioned in the following sections.

Other Results: 1) In our last year's report we mentioned studies of delocalized excitations in ZnS doped with Cu^+ and Ag^+ impurities. We have brought these studies to a conclusion and combined them with studies on mixed ZnS-CdS phosphors to provide a conclusive test of the donor-acceptor theory of these phosphors. Our results are entirely in accord with the theory. We have further studied the effect of pressure on the peak shift and emission intensity for purely localized excitations in ZnS doped with Mn^{++} and Pb^{++} . We were able to relate the emission energy, intensity, and lifetime in a quantitative manner, consistent with theory.

2) We have perfected a technique for increasing the effect of pressure to 12 kilobars on fluorescence depolarization. In studies of small molecules like fluorescein, we show quantitatively consistent results between pressure data and temperature data.

For a polymer (polyvinyl naphthalene), there is a large temperature effect on the depolarization but almost no pressure effect. This shows that the depolarization is not a viscosity effect as previously supposed but is a thermally activated process internal to the molecule. We plan extensive studies on a variety of polymers.

3) One of the central problems of photophysics and photochemistry is the energy of triplet states relative to excited singlet states. The possibility of intersystem crossing to the optically unavailable triplet state and subsequent dissipation of the energy by optical, thermal or chemical pathways is of great importance both for fluorescence efficiency and photochemical reactivity. Molecules like 9-anthraldehyde and its derivatives exhibit almost no fluorescence because they are quenched by intersystem crossing. Pressure tends to decrease the energy of the excited singlet states of aromatic molecules relative to the ground state because of the relatively large polarizability of the excited state. Because of the requirements of the Pauli principle, triplet states are much less polarizable and should thus increase in energy with pressure relative to the excited singlet and so become less available for intersystem crossing. Our pressure experiments indicate that the fluorescence efficiency of these compounds increases by three orders of magnitude in 100 kilobars, as our analysis would predict.

Results Expected FY79: 1) New Experimental Techniques. With equipment now on order, we expect to extend our capacity to measure fast lifetimes and weak signals. With our new flash lamps, we will be able to resolve lifetimes as fast as 4-5 nanoseconds instead of our present limit of 50-60 nanoseconds. We shall also be able to resolve peaks as weak as 10^{-6} quantum efficiency instead of our present limit of 5×10^{-6} .

2) Continuing Experiments. We plan to continue the work in several of the areas mentioned above:

(a) We expect to intensify our study of the nature of the triplet state in systems of π^* orbitals and should substantially complete our characterization.

(b) We propose to continue and expand our studies of viscosity effects on optical processes to include isomerization, energy transfer and excimer formation. We plan to combine peak location and intensity measurements with lifetime studies using our new lamp, and, in collaboration with Professor K. Kaufman, extending measurements into the picosecond range. We expect two or three finished projects but this phase of the work has ramifications which will extend over several years.

(c) We expect to extend our fluorescence depolarization studies to include new classes of polymers with fluorescent peaks strategically located on side chains, at crosslinks, etc. We plan to finish a number of subprojects but this, again, will continue at least into 1980-81.

3) New Projects. We plan to initiate a number of new projects. We mention several here where preliminary work indicates that substantial results can be expected in FY79.

(a) A year ago we published a definitive paper on energy transfer in crystals by the dipole-dipole mechanism. We are initiating a study of the exchange

mechanism at this time. We plan first to study exchange transfer from Sb^{+3} to Mn^{+2} in halophosphate lattices. The crystals were obtained from General Electric and are of the type used in fluorescent lighting. We plan to extend the studies to other systems and believe we can perform as complete a test of the theory as we did for dipole-dipole processes.

(b) We plan to study ligand to metal energy transfer in a series of Eu^{+3} doped oxysulfide lattices. Preliminary work indicates large perturbations of the ligand states with pressure with little or no effect on the f-f transitions in Eu^{+3} . Thus, large changes in efficiency and lifetime are observed. The crystals were obtained from RCA and are important in laser design and for lamp applications. We shall alternatively extend our studies to other systems where exchange is important.

(c) In aromatic molecules containing nitrogen or oxygen, excitations can occur to antibonding π^* either from bonding (π) levels or from nonbonding (n) levels. The characteristics of the excited molecule as regards rates of internal conversion, intersystem crossing, fluorescence and chemistry depend strongly on the degree of $n-\pi^*$ or $\pi-\pi^*$ excitation involved. We find with pressure that we perturb $\pi-\pi^*$ excitations more than $n-\pi^*$. By a combination of intensity and lifetime measurements, we can probe excited molecules and determine the kind of excitation which is dominant.

(d) Rare earth and transition metal ions form chelates with a variety of organic ligands. These compounds are important in homogeneous catalysis and in chemical synthesis. Frequently one can absorb light in the ligand which transfers the energy to the metal ion so that emission from an excited state to the ground state of the metal ion occurs. This process is very sensitive to the energy of the excited ligand relative to the excited states of the metal ion. In many such molecules the ligand levels are much more strongly perturbed by pressure than is the metal ion so that the efficiency of the energy transfer process is very sensitive to pressure. Since the ligand itself frequently does not emit, studying the emission of the metal ion as a function of pressure gives a direct probe of the effect of pressure on the ligand levels. We plan to start with some rare earth acetylacetonate chelates and extend the study to other ligands and metal ions.

(e) Electron donor-acceptor complexes are of considerable interest in chemistry, physics and biology (TTF-TCNQ is an example of such a complex). Optical excitation occurs from a predominantly donor level to an excited state which is a mixture of donor and acceptor states. Emission may come from this state or after transfer to an excited state of the acceptor or from a triplet state either of the acceptor or the complex. These various excited states are perturbed by pressure in significantly different degrees, so that pressure studies of emission spectra, intensity and lifetime will contribute in an important way to the characterization of this interesting and important class of materials.

Results Expected FY80: The basic thesis of our work has been, and is, the essential nature of pressure for understanding electronic phenomena in condensed systems. We have, over the years, used a wide variety of probes to investigate electronic phenomena. In the past two years we have developed considerable expertise in studying luminescent phenomena at high pressure--peak locations, intensities, and lifetimes. We are finding this area considerably more fruitful than we had anticipated and we expect to be exploiting it for a number of years. Problems involving luminescent efficiency, energy transfer, and photochemistry have a variety of applications in the energy field, as we have discussed above. The availability of equipment to measure very fast lifetimes and very low intensities makes possible not only more accurate or more sophisticated measurements, but whole new types of studies. Some of these are noted under (19) above. Other possibilities include the separation of rare earth or transition metal ions by photochemical means in solution, photoconductivity and photochemistry of transition metal ions, especially iron, in solution, with implications for corrosion, and photoconductivity of charge transfer processes. In all these cases, the ability to perturb the properties of the medium in a controlled way makes high pressure an ideal tool for gaining a better understanding of phenomena.

Relationship to Other Projects: There is really no other laboratory in the world which duplicates any significant fraction of our studies on pressure and electronic structure. McWhan and Jayaraman at Bell Labs have made a significant contribution in the area of insulator-metal transitions. Offen at Santa Barbara and Nicol at UCLA have performed a number of important studies of organic phosphors. Our research has been used extensively by theoreticians in physics, chemistry, and geophysics for testing the analyses which they have developed.

Over the years, we have collaborated with people in a variety of fields, and these collaborative efforts appear to be on the increase. The most valuable has been the continuing interaction with C. P. Slichter of the Physics Department which has led to a real understanding of the nature of a variety of electronic transitions. Earlier cooperation with H. Frauenfelder and P. Debrunner of the Physics Department was very valuable in developing high pressure Mössbauer resonance techniques. Gregorio Weber, Professor of Biochemistry and Biophysics, is the moving spirit behind our very interesting and fruitful studies of protein denaturation. G. Schuster, Assistant Professor of Organic Chemistry, is working intensively with us on various aspects of high pressure photochemistry, and his suggestions and assistance with syntheses have been extremely valuable. We interact almost daily with J. Jonas, Professor of Physical and Analytical Chemistry. We plan some direct collaborative work, but the relatively subtle contributions spanned by this continuous interaction far exceed the limits of any particular projects.

Our expertise contributes in an indirect way to a continuing interaction with the catalyst group and the solar physics group at the Corporate Research Labs of Exxon Research and Engineering.

Publications (Calendar Year 1977):

K. W. Bieg and H. G. Drickamer

A High Pressure Test of the Theory of Energy Transfer by Sensitized Luminescence

J. Chem. Phys. 66, 1437-1441 (1977)

K. W. Bieg and H. G. Drickamer

Effect of Quadratic Electron-Phonon Interaction on Band Shapes

J. Appl. Phys. 48, 426 (1977)

K. W. Bieg, D. L. Woracek, and H. G. Drickamer

High Pressure Luminescence Studies of Alkali Halide Phosphors Doped with Pb^{++} and Sn^{++}

J. Appl. Phys. 48, 639-646 (1977)

L. A. Brey, G. B. Schuster, and H. G. Drickamer

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Chem. Phys. Lett. 47, 462-465 (1977)

E. N. Hockert and H. G. Drickamer

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Biochemistry 16, 4883-4886 (1977)
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High Pressure Studies of Electronic Phenomena
Proceedings of the Sixth International Conference on High Pressure
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and Technology, Boulder, CO, July 1977) (to be published)

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 High Pressure Luminescence Studies of Indole and 5-Methoxyindole in
 Polymethylmethacrylate
 J. Chem. Phys. (submitted to)

J. W. Hook, III and H. G. Drickamer
 High Pressure Studies of Thermoluminescence of Doped ZnS Phosphors
 J. Appl. Phys. (in press)

D. Klick and H. G. Drickamer
 High-Pressure Studies of Jahn-Teller Split Luminescence in Alkali Halides
 Doped with In^+ and Tl^+
 Phys. Rev. (in press)

G. S. Chryssomallis, H. G. Drickamer, and G. Weber
 The Measurement of Fluorescence Polarization at High Pressure
 J. Appl. Phys. (submitted to)
 Also supported by USPH Grant GM-11223

Theses (Calendar Year 1977):

E. N. Hockert (H. G. Drickamer, Adviser)
 Effects of High Pressure on the Photochromism and Thermochromism of the Anils
 Ph.D. Thesis

J. W. Hook, III (H. G. Drickamer, Adviser)
 High Pressure Luminescence Studies
 Ph.D. Thesis

G. L. House (H. G. Drickamer, Adviser)
 Effects of High Pressure on the Luminescence Properties of Zinc Sulfide
 Phosphors
 Ph.D. Thesis

D. I. Klick (H. G. Drickamer, Adviser)
 Luminescent Decay and Spectra of Impurity-Activated Alkali Halides Under
 High Pressure
 Ph.D. Thesis

C. E. Tyner (H. G. Drickamer, Adviser)
 Effects of High Pressure on Thermal Quenching of Luminescence
 Ph.D. Thesis

G. Chryssomallis (H. G. Drickamer)
 The Effect of Pressure on the Polarization of Organic Molecules in Solution
 M.S. Thesis

Impurities in Superconductors

Principal Investigator: Donald M. Ginsberg, Ph.D.
Professor of Physics
Associate Head, Department of Physics

Supporting Agency: U. S. Department of Energy

Senior Staff: Donald M. Ginsberg, Professor

Junior Staff: Brian C. Gibson, Research Assistant
Bradley W. Nedrud, Research Assistant

Object: We are exploring the effects of two types of impurities on the properties of superconducting materials. One type (Project A) is hydrogen, and the other (Project B) consists of magnetic impurities.

Project A. The effect of hydrogen doping on the properties of materials has become a topic of widespread interest. Some of the most dramatic effects of hydrogen have been observed for superconductors. For example, palladium, which is not a superconductor at all when it is pure, can be made to become superconducting at a temperature of 9 K by adding hydrogen, or can be made superconducting at even higher temperatures (up to 16 K) by adding hydrogen with copper, silver, or gold. It has also been observed that hydrogen produces anomalies in the thermal conductivity of niobium and tantalum, and in the specific heat of vanadium, niobium, and tantalum in the superconducting state.

Many mechanisms have been suggested to account for these effects. Among these mechanisms are: (a) a reduction of normal-state fluctuations, (b) a change in the electronic density of states, (c) phonon mode softening, and (d) a change in the electron-phonon coupling strength. The interpretation of experimental results is sometimes complicated by precipitation at high doping levels.

We are investigating the influence of hydrogen doping on the superconducting properties of quench-condensed films of indium and lead. The metals and the hydrogen are simultaneously condensed onto a cold (2 K) substrate. In these samples, spin fluctuations and precipitation are not expected to be present. (The samples could also be made by ion implantation, but this method yields very inhomogeneous samples, so we avoid it.) By performing electron tunneling measurements and analyzing the results, both the phonon and electron densities of states and the electron-phonon coupling constant will be determined. The superconducting transition temperature and resistivity of each sample will also be determined.

The data will enable us to begin to truly understand how hydrogen affects the properties of superconductors. Ultimately, this understanding could help to develop superconductors with high transition temperatures. The technological importance of such a development for energy production, distribution, and utilization are self-evident.

Project B. Magnetic impurities have a very strong influence on the properties of superconductors. For technological purposes, the most interesting effect is the shift in the critical magnetic field. This shift, although usually downward, can be upward, by as much as 100 kilogauss, because of antiferromagnetic coupling between the impurity atoms and the conduction electrons. By pursuing a basic study of the influence of magnetic impurities on the properties of superconductors, our understanding of these effects may be increased to the point where such improvements in superconducting properties can be systematically guided. It is also important to investigate the ways in which superconducting properties are sometimes degraded by magnetic impurities, so we will know how pure materials should be to avoid some of the undesirable effects which are sometimes observed.

One avenue of approach which we are following is to investigate the influence of magnetic impurities from among the 3d elements of the periodic table. These impurities have a comparatively large influence on the superconducting electrons; the theoretical treatment of this influence cannot rely on perturbation theory and is, therefore, in a somewhat undeveloped state. In conjunction with thermal conductivity, critical field, and critical temperature data which we have already acquired, we are now amassing specific heat data, and we plan to obtain electron tunneling data as well. The materials are films of indium and lead, doped with manganese and chromium. In these materials, very small amounts of the magnetic impurity are sufficient to create the observed effects, and side effects which might be introduced at larger doping levels are therefore avoided. When all of our data are in hand, we will have a very complete picture of the fundamental properties of these materials, and the theories which we have (those of Shiba and of Müller-Härtmann and Zittartz) can be tested definitively. Possible lines along which the theories should be improved may be indicated by our results.

Another avenue of approach which we will follow is the investigation of dilute alloys containing uranium impurities. Uranium intermetallic compounds have recently attracted considerable interest by those who are investigating the formation of magnetic moments in metals. There is a possible influence of direct f-f and f-d interactions, yielding itinerant behavior. In general, compounds in which the separation between uranium atoms is small tend to be either superconducting or paramagnetic, i.e., they exhibit itinerant behavior, whereas compounds in which that separation is large tend to have localized magnetic states and to order magnetically. These rules are sometimes violated, however, so interconfigurational fluctuations may also be important. We plan to perform a systematic series of measurements of magnetic susceptibility, superconducting transition temperature, critical magnetic field and electrical resistivity. Our results will be interpreted in conjunction with measurements of specific heat, thermopower, and neutron scattering which will be carried out by cooperating groups at the University of Cologne and at Grenoble. This broadly based investigation should enable us to reach definite conclusions about the magnetic behavior of uranium atoms in superconductors, and may help us to understand related materials as well.

Results FY78:

Most Significant Accomplishments: Project B. We have made a complete set of measurements of ΔC , the jump in the electronic specific heat which occurs at the superconducting transition, in films of indium doped with various amounts of manganese. The results are of sufficiently high precision to show that the theory of magnetic impurities in superconductors must include either (a) p-wave and/or d-wave scattering in addition to s-wave scattering or (b) proper quantum-mechanical treatment of the noncommutation of different components of the impurity spin (Kondo effect): The observed values of ΔC are somewhat too small to agree with the classical theory (by Shiba) if only s-wave scattering is included. We have begun to perform ab initio calculations, including p-wave and d-wave scattering, with the help of Professor A. B. Kunz, to begin to sort out the possible explanations for this situation.

Other Results: Project A. We have acquired preliminary tunneling data on hydrogen-doped indium which indicate that the superconducting transition temperature T_c and the order parameter Δ of indium are increased by the presence of hydrogen. An increase in the ratio $2\Delta/k_B T_c$ is also observed, indicating increased electron-phonon coupling. These conclusions are still tentative, however. We have partially completed our work to automate this experiment.

Results Expected FY79: Project A. We will finish automating our experiment so we can acquire a large amount of tunneling data for detailed computer analysis by McMillan's well-known program. This will yield the electron and the phonon density of states and the electron-phonon coupling constant. We must also improve our sample preparation techniques to control better the rate at which the metal is evaporated from the hot source and condensed onto the substrate. This will give us better control of the sample's doping level, and better homogeneity of the doping level. These improvements, together with the job of learning how to perform the computer analysis, will probably require most of the year. Serious data acquisition can also begin.

Project B. We will conclude our specific heat experiment by acquiring data on a series of lead-manganese alloys and writing up our results.

We will begin performing tunneling measurements on indium-manganese and lead-manganese samples.

We will set up the equipment for making measurements of the magnetic susceptibility, critical temperature, and critical field of dilute alloys containing uranium. The measurements should be well under way in this time period.

Results Expected FY80: Project A. We hope to be able to obtain the remaining data to complete this tunneling measurement and to analyze the data. We may be able to begin investigation of the influence of deuterium on the properties of superconductors.

Project B. We will continue to perform tunneling measurements on indium-manganese and lead-manganese samples. If time permits, we will also investigate indium-chromium samples. We will compare the results with theory, both the s-wave-only theory and the theory including higher-order partial wave scattering of the electrons from the impurities.

We will conclude our measurements on dilute uranium alloys. The direction of future work in this area will then be determined, depending on our conclusions.

Relationship to Other Projects: Our work is related to investigations here (in Professor C. B. Satterthwaite's group) and at the Argonne National Laboratory (by Dr. T. Brun and his coworkers) on the influence of hydrogen on the properties of superconducting transition elements. The work at Argonne includes neutron scattering, which is a very powerful technique. The electron tunneling measurements which we are making are also based on a very powerful technique, but one which is extremely difficult to perform on the transition elements. The difficulty stems from the very short superconducting coherence length in the transition elements: Tunneling measurements determine the properties of the superconductor within a coherence length of the surface. If the coherence length is very small, the surface conditions are of critical importance. As a result, reliable superconducting tunneling measurements have not been obtained for the transition metals to date. Thus, our work and the work on the effect of hydrogen on the transition metals are complementary attacks on the same fundamental problem.

Publications (Calendar Year 1977):

J. W. Thomasson and D. M. Ginsberg
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Phys. Rev. B15, 4270-4271 (1977)
Also supported by National Science Foundation Grant DMR-76-01058

D. M. Ginsberg
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Phys. Rev. B15, 1315-1317 (1977)
Supported by National Science Foundation Grants DMR-72-03026 and DMR-73-07581

John X. Przybysz and D. M. Ginsberg
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Phys. Rev. B15, 2835-2836 (1977)
Supported by National Science Foundation Grants DMR-72-03026 and DMR-73-07581

Theses (Calendar Year 1977):

James W. Thomasson (D. M. Ginsberg)
Electromagnetic Penetration Depth in Superconducting Alloys Containing
Magnetic Impurities
Ph.D. Thesis
Also supported by National Science Foundation Grants DMR-72-03026, DMR-73-07581,
and DMR-76-80159

Ultrasonic Studies of the Structure of Matter

Principal Investigator: Andrew V. Granato, Ph.D.
Professor of Physics

Supporting Agency: U. S. Department of Energy

Senior Staff: Andrew V. Granato, Professor
George G. Setzer, Research Assistant Professor

Junior Staff: David L. Johnson, Research Assistant
Gary A. Kneezel, Research Assistant (until 01/05/78)
David B. Poker, Research Assistant
Humphrey P. Wong, Research Assistant

Object: This research program uses the unique capabilities of ultrasensitive ultrasonic techniques to investigate the structure of interstitial atoms in metals (including hydrogen in metals), to determine the role of dislocations in determining the strength of metals, and measure nonlinear elastic properties which determine the thermal behavior of solids. The phenomena under investigation are all of central importance for the use of metal structures under extreme conditions of temperature, stress, and hostile environments which induce contamination by point defects. The projects undertaken fall within the areas of interest to DOE of radiation damage, hydrogen in metals, superconductivity, and equations of state.

A) Interstitials in Metals. We are studying the structure of point defects produced during radiation and annealing of metals. The structure is deduced from the anisotropy, relaxation and resonance type behavior of elastic constant changes produced by radiation damage. The information is basic to the understanding of how defects combine to produce large agglomerates. Interstitial-impurity (mixed-dumbbell) complexes, which have important applications in the analysis of swelling in reactor materials, are under study. The same techniques are being used for the study of the structure of hydrogen and deuterium in metals. A determination of the symmetry of H and D in Nb is of importance for the checking of recently proposed quantum models for the disposition of hydrogen in bcc metals.

B) Strength of Crystals. Amplitude dependent attenuation and velocity changes are used to study unusual strength effects. Traditional theories of strength have been based upon rate theory assuming explicitly that the overcoming of obstacles is the rate-limiting step. Implicit assumptions in this approach are that the dislocations do not overshoot the obstacles by reason of their inertia and that the time taken to travel between obstacles is not rate-limiting. We are studying materials for which these implicit assumptions do not appear to be valid.

C) Nonlinear Elastic Effects. Many thermal properties of solids depend upon deviations from linear elastic behavior. We are measuring the temperature

dependence of elastic constants at low temperatures where the elastic constant changes can be used to determine third and fourth order elastic constants. This data is of use in determining useful empirical interatomic potentials and equations of state.

Results FY78:

Most Significant Accomplishments: We have developed a theory for the strength of dilute alloys which takes dislocation inertial effects into account. The theory is based on an analogy of dislocation behavior with the Brownian motion of a particle, and can be used to explain the strength loss observed in metals entering the superconducting state, as well as the anomalous maximum observed in the flow stress of dilute alloys at low temperatures. According to the theory, whenever the product of the viscous damping B and the average dislocation free segment length L is less than a critical value, dislocations which overcome barriers thermally can inertially overshoot subsequent barriers. This increases the average plastic strain per thermally activated event. The theory explains in a natural way how one can have both the mechanical and rate effects observed occurring simultaneously.

Other Results: 1) The full set of elastic constants of niobium containing oxygen and hydrogen has been measured between 0.5 and 10 K. Specimens containing hydrogen show two relaxations. One relaxation frequency is at 10 MHz at 2.5 K while the other is at much higher frequencies. The system has a symmetry which is such as to produce no effect for C_{44} type modes. When measurements with deuterium are completed, the results will be used to try to determine models for the hydrogen configuration.

2) Amplitude dependent internal friction measurements have been used with our recently developed theory to deduce information about distributions of obstacle strengths in dilute alloys. Results for pure and 1000 ppm lead alloys look reasonable and indicate that this may become a practical technique.

Results Expected FY79: 1) We expect to obtain detailed information concerning the configuration of hydrogen in niobium. Measurements of elastic constants and decrement as a function of orientation, temperature, frequency, concentration, isotope and impurity content are in progress. High sensitivity decrement measurements have recently been added to complement the high sensitivity elastic constant measurement technique already developed. It is expected that the results will be sufficiently detailed to permit discrimination among different models which have been proposed for the quantum diffusion behavior of hydrogen in niobium.

2) We expect to obtain results for the behavior of mixed dumbbell interstitials in a series of crystals of aluminum with different impurities. Measurements will be made of both the in-phase and out-of-phase elastic response as a function of orientation, frequency, temperature, concentration and type of impurity. Measurements are in progress in the Al-Mn system, to be followed by Al-Fe and Al-Zn. It is expected that each impurity will lead to a different dielastic

and paraelastic response, leading to an ultrasonic spectroscopy of such systems. It is hoped to measure the resonant frequency and coupling strengths of the defects, as well as the activation energies of their motions. Computer calculations of the configuration and motions of the defects will also be made.

3) We plan to develop further equation of state models using nonlinear elastic data from different crystalline systems.

Results Expected FY80: 1) We expect to make studies of interstitial configurations in bcc and hcp materials, using techniques similar to those presently in use for fcc materials. Measurements using x-ray scattering and Mössbauer effects have confirmed the configuration we first found for the free interstitial in fcc materials, as well as the resonance modes of such defects. However, the situation is less clear in bcc materials, where different techniques have produced different conclusions.

2) We expect to make studies of interstitial-impurity complexes, similar to those presently under study in fcc materials, in a wider class of materials including bcc metals. Because of the better understanding currently existing for fcc metals, we hope to establish for fcc metals first the ultrasonic techniques as a useful method of obtaining information about such complexes. When this is done, we wish to turn to bcc metals, which are of special importance in applications for swelling in reactor materials.

Relationship to Other Projects: Our hydrogen in niobium project is a collaboration with H. K. Birnbaum of this Laboratory. Also, we collaborate with J. Holder of this Laboratory on radiation damage studies, and also on some aspects of Holder's project on the deformation of ice crystals. We are in close touch with L. Rehn, a former student here, who has initiated a project at Argonne Laboratories of elastic constant studies of mixed dumbbell interstitials.

Publications (Calendar Year 1977):

R. B. Schwarz

Simple System Using One-Crystal Composite Oscillator for Internal Friction and Modulus Measurements

Rev. Sci. Instrum. 48, 111-115 (1977)

R. B. Schwarz, R. D. Isaac, and A. V. Granato

Dislocation Inertial Effects in the Plastic Deformation of Dilute Alloys of Lead and Copper

Phys. Rev. Lett. 38, 554-557 (1977)

Also supported by National Science Foundation Grant DMR-77-10556

A. V. Granato

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A. V. Granato

Dislocation-Phonon Interactions

Proceedings Sixth Int. Conf. Internal Friction and Ultrasonic Attenuation
in Solids, Japan, 1977, J. Phys. Soc. Japan (in press)

Also supported by National Science Foundation Grant DMR-77-10556

D. M. Joncich, A. V. Granato, and J. Holder

A Direct Determination of an Upper Limit for the Electrical Charge on
Dislocations in Ice

J. Glaciology (submitted to)

Also supported by National Science Foundation Grant DMR-76-01058

Theses (Calendar Year 1977):

R. D. Isaac (A. V. Granato, Adviser)

Thermally Activated Dislocation Motion Including Inertial Effects in Solid
Solutions

Ph.D. Thesis

Defect Properties of Solids

Principal Investigator: David Lazarus, Ph.D.
Professor of Physics

Supporting Agency: U. S. Department of Energy

Senior Staff: David Lazarus, Professor
Marjorie P. Yuhas, Research Associate

Junior Staff: Genghmun Eng, Research Assistant
James N. Oberschmidt, Research Assistant
Arthur E. Pontau, Research Assistant

Object: This research program is concerned with defects in solids, where the word "defect" encompasses a variety of departures from the ideal, perfect, monatomic lattice: thermally-induced defects, such as vacancies and interstitials; structural defects, where missing or extra sites are inherent to the crystalline lattice itself; electronic defects, such as impurities, which perturb the local lattice. The chief emphasis of the program is to develop quantitative, atomistic models for such defects in classic, prototypic solids. It is hoped that this will lead to useful structural and electronic materials which can operate in extreme environments.

In many applications, the utility of materials is limited severely by inherent and thermally-induced defects. These give rise to plastic flow, corrosion, phase changes, embrittlement, wear, fatigue, etc. Associated with each of these phenomena is the atomistic process of diffusion within the solid matrix, and one of the chief goals of this research has been to develop atomistic models for the diffusion process in a wide variety of solids, metals as well as insulating materials. We would like to understand what governs diffusional rates, why host atoms and impurities migrate at different speeds, how temperature and stress affect diffusional behavior, why many materials exhibit comparable diffusivities at homologous temperatures relative to the melting temperature, while others show differences of orders of magnitude.

Much of our previous work has been concerned with identifying the structural and electronic interactions of defects which govern mass transport in simple ionic crystals, such as NaCl, and fcc metals, such as noble metals. In all such cases, the basic defects responsible have been shown to be predominantly the thermally-induced monovacancy. Other studies have shown that the monovacancy also governs diffusion in most bcc metals, while interstitial motion is dominant in silver halides. Much of our current work centers around cases of "anomalous" diffusion: in some of the bcc refractory metals, such as Ti, Zr, Hf, and U; in "superionic" conductors such as AgI and PbF₂; even in "understood" materials like NaCl when the diffusing constituent is aleovalent to the lattice. We are trying to determine whether the anomalies are understandable in terms of classic vacancy or interstitial mechanisms, or if new mechanisms must be invoked.

To resolve these issues, precise measurements of diffusion must be made, using radiotracer techniques of high accuracy and/or conductivity measurements in ionic solids, to determine precise values of the diffusivity of various host and impurity atoms as functions of temperature, pressure, isotopic mass, valence, etc. Temperature measurements suffice only to permit evaluation of characteristic enthalpies for formation and motion of defects. Pressure measurements yield values of defect volumes, while mass dependence measurements yield measures of the nonrandomness of successive atomic jumps. It is only by a combination of these techniques that a detailed atomic description can be achieved of the formation and motion of the underlying defects associated with mass transport.

The electronic configurations surrounding impurity atoms must be understood in order to derive models for the differences in diffusivity of host and impurity atoms, as well as the effect of impurities and structural defects on the electronic and magnetic properties of solids. Measurement of the effects of large hydrostatic pressures on electronic and magnetic properties of pure metals and alloys gives a sensitive test of theoretical models, since the pressure induces only a simple, uniform lattice change, essentially a simple volumetric scaling operation. These methods have proven useful in earlier studies of thermoelectric properties and Fermi surfaces. Current work is centered about elucidating the electronic structures of mictomagnetic and spin-glass materials, typified by CuMn alloys of varying composition.

Results FY78:

Most Significant Accomplishments: A more general solution has been found to analyse the problem of nonlinear diffusion in insulating materials caused by migration of aleovalent impurities. Mathematically, the nonequilibrium case is treated by use of Hermite polynomials to propagate the diffusion profile via the nonseparable second-order differential equation from its shape at a diffusion time t_1 to that at a later time t_2 . Physically, this involves measurement of tracer profiles from identical initial conditions in a set of crystals which are annealed for varying times at the same temperature. Since the initial state is a diffused profile rather than a sharp delta-function tracer layer, the effect of aleovalent impurities on the vacancy concentration is "diluted" and a valid solution can be found for more extreme cases. The theoretical work has been confirmed by measurements of tracer diffusion of Ca in NaCl.

Other Results: Measurements have been made of the effect of pressure on the electrical resistivity of mictomagnetic Cu₇₈Mn₂₂ alloys, over a temperature range 4-400 K. These measurements indicate that the decrease in lattice parameter, caused by pressure, effects a ten-fold increase in resistivity above that due simply to dimensional changes. The effects are the same for quenched, annealed, and cold-worked samples. Work has been started to see if similar effects are found for Cu₉₅Mn₅ spin-glass and intermediate compositions.

First results of diffusion in TiNb alloys show a systematic variation of the correlation factor with Nb concentration, but no major anomalies due to suppression of the alpha-beta transition. Values of the correlation factor deduced by the Manning formalism are consistent with a vacancy mechanism. Attempts to study the effects of prolonged pre-diffusion anneal on diffusion in Ti proved unsuccessful due to problems of contamination of the Ti by aluminum from the furnace tubes and by simple sublimation of the Ti samples themselves in high vacuum at temperature. The work will be continued using Zr, which has a far lower vapor pressure, and with an intermediate enclosure of Zr to obviate contamination by impurities from the ceramic furnace tube.

Work has begun on two other projects: a) a study of the effects of pressure on the high-temperature conductivity of fluorite crystals, some of which exhibit superionic behavior following a continuous rise from a normal low-temperature state (with no first-order transition), and some of which remain essentially normal to the melting point; b) a study of tracer diffusion of Ag in RbAg_4I_5 --an exceedingly difficult experiment because of the enormous diffusivity of Ag even at room-temperature ambient temperatures in the superionic phase. Handling and tracer deposition will all have to be done at liquid nitrogen temperatures, and apparatus is currently being developed to permit all tracer deposition and sectioning procedures to be carried out on pressed-pellet samples at low temperature.

Results Expected FY79: The present studies of diffusion in TiNb alloys and RbAg_4I_5 should be completed. The work on diffusion in Zr and ionic conductivity in fluorites should be nearing completion. A program of measurement of susceptibility in CuMn alloys may be undertaken, if the resistivity studies completed in FY78 are not sufficient to provide a theoretical understanding of the effect of pressure on the magnetic interactions.

Results Expected FY80: The program of diffusion in Zr and high-pressure ionic conductivity in fluorites should be completed. New diffusion studies may be undertaken in oxides and other superionic materials.

Relationship to Other Projects: Some of our research is conducted in collaboration with other principal investigators within MRL, and in other departments of the University. Our studies of superionic solids complement those of M. V. Klein and M. Salamon. We have also collaborated with N. Holonyak, of the Electrical Engineering Department, in studies of light-emitting semiconductor materials. C. A. Wert and P. Beck, of the Department of Metallurgy, have collaborated in studies of diffusion in metals and in properties of magnetic alloys. Work on dichalcogenide crystals has been done in cooperation with F. C. Brown and M. Salamon. We have also collaborated with H. Frauenfelder of the Department of Physics in measurements of pressure effects of the kinetics of biological processes.

None of our work directly duplicates that done anywhere else in the U.S., or the rest of the world. We maintain close relationships with other groups by

exchange of preprints and reprints, letters, meetings, and visits. Workers in the field of diffusion are widely dispersed in the U.S., and in the rest of the world. Active contacts are maintained, particularly with groups at Argonne National Laboratory, University of North Carolina, Rensselaer Polytechnic Institute, Cornell, and Harvard, in the U.S.; with groups at Saclay and Bellevue, in France; with groups at Munster and Berlin in W. Germany; with a group at Gothenberg, Sweden; Tokyo and Kyoto, Japan; Athens, Greece; Cambridge, Reading, and Oxford, England; and even, on occasion, one or two within the USSR.

Publications (Calendar Year 1977):

Mark S. Jackson and David Lazarus
Isotope Effect for Diffusion of Tin in Beta-Titanium
Phys. Rev. B15, 4644-4656 (1977)

Paul C. Allen and David Lazarus
Effect of Pressure on Ionic Conductivity in Rubidium Silver Iodide and Silver Iodide
Phys. Rev. B (accepted for publication)

Theses (Calendar Year 1977):

P. C. Allen (D. Lazarus, Adviser)
Effect of Pressure on Ionic Conductivity in Rubidium Silver Iodide and Silver Iodide
Ph.D. Thesis

Properties of Crystalline Condensed Gases

Principal Investigator: Ralph O. Simmons, Ph.D.
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Object: The research being conducted and proposed has four themes. First is to investigate solid-solid phase transitions which, amidst other physical property changes, account for the absorption and release of energy in systems such as solid hydrogen and solid methane. Second is to clarify the understanding of lattice anharmonicity in electrical insulators. The importance of anharmonicity is that it provides a mechanism for the transport of heat and it gives rise to thermal expansion, to temperature dependence of the elastic properties, etc., factors which are important to energy systems. Third is a goal to determine the structure of thermal defects in the crystalline heliums and to elucidate the mechanisms by which atomic diffusion takes place, by a regime dominated by quantum effects. The heliums are chosen as model systems exhibiting extremely large effects, systems from which one may learn new insights about atomic mobilities in materials. Finally, a fourth goal is to explore certain phenomena in monatomic solids in the immediate neighborhood of melting, over a range of pressures. Condensed gases are chosen as the solid materials for investigations of the present program because the phenomena arise, in such materials, in extreme form, better separated from other effects. The phenomena can be precisely studied over an especially large range of physical conditions: factors of more than a hundred in temperature and changes up to 40 percent in solid density. Another significant advantage of these materials, as model systems for the study of solid state phenomena, is the relative ease of controlling their purity and precisely analyzing their impurity content. Finally, isotopic substitution can be used to separate physical and chemical effects and to prove alternative atomic mechanisms.

To pursue these goals, using these materials, continues to require the invention of new types of apparatus. Adaptations of the techniques developed continues by other scientists, giving them the means to carry out research in other areas of materials science.

The first goal, characterization of some solid-solid phase transitions due to molecular rotational ordering, is intended to form a testing ground for modern theories of phase transitions. The circumstances are complex, but the number of variable features is limited and controllable. Solid hydrogen and deuterium, including mixtures of the species ortho- and para- in each

case, exhibits a rich set of excitations, which are coupled to one another in challenging fashion. The solid methanes are also attractive model systems for these purposes. Certain systematic features are exhibited in the phase transitions of the five different deuterated methanes and of the mixtures of CH_4 and CD_4 . The molecules have a simple electron closed-shell configuration. The influence of total nuclear spin on macroscopic crystal properties is large, and molecular rotational moments of inertia can be varied over a broad range. A wide variety of experimental techniques can be applied: x-ray, neutron, NMR, optical, calorimetric, dielectric, and spectroscopic.

The practical importance of the second goal, understanding anharmonicity in insulators, has already been emphasized. Applications of solid materials in technology, not only for mechanical construction but also for component elements in solid-state electrical devices, often depend upon the thermal properties of these materials. Advances in the microscopic understanding of anharmonicity are confined to the last decade. Our own interests in this area include not only thermal expansion studies but also are focused on phenomena in the immediate neighborhood of melting, over a range of densities, where one hopes to get new insights into the short-range interactions between atoms.

Pursuit of the third goal merits a longer description. The literature of diffusion in solids contains speculations about many possible mechanisms and accounts of measurements using many physical probes of atomic jumping processes. By now, atomic mobility is understood phenomenologically in many well-characterized classical systems. Such mobility is exploited (or cursed!) in the behavior of many solid materials of importance to technology. Recently, interest in quantum manifestations of atomic mobility in solids has grown. Model systems chosen for scientific, not technological reasons, are useful in exploring more readily the full range of real possibilities which may need to be invoked in understanding, and possibly controlling, atomic mobility in materials.

The most extreme cases of atomic mobility occur in solid helium, especially bcc ^3He at low densities. Crystalline binding is so weak, and the atoms are so light, that atomic mobility is easily measurable even in the limit of extreme low temperature. Quantum excitation of atomic mobility shades, at higher temperatures, into thermal excitation. Because of the great compressibility of this material, studies can be conducted over a large range of interatomic interaction strengths, without chemical alterations.

For this research program, methods have been developed for directly measuring defect content in crystals, both at low pressures and, for the first time in any solid, at pressures great enough to permit the volume-dependence of thermal defect properties to be determined. The contributions of thermal defects to a variety of physical properties of solids have also been established.

The fourth goal for this program arose as a possibility when ultra-precise x-ray V-T studies on argon and krypton confined at pressures up to 200 MPa showed apparent rapid variation in thermal defect content of the solid in the immediate neighborhood of the melting line. The phenomena, which may relate to microscopic features of the melting process, deserve further examination.

Results FY78:

Most Significant Accomplishments: The fcc to hcp and hcp to fcc phase transitions in mixtures of ortho- and para-H₂ have been followed directly by x-ray diffraction from single-crystal specimens at temperatures down to 130 mK. At temperatures at 1 K and above, the results agree well with previous x-ray, calorimeter, NMR, and dP/dT studies. Contrary to previous expectation of NMR workers, however, the structure transitions below 0.6 K occur at ortho-concentrations near 50%, not lower. NMR and IR searches for (quadrupolar) spin glass behavior, and the applicable theories, evidently need to be based on new assumptions.

Work on pure crystalline argon, krypton, and xenon has established x-ray lattice parameters along the melting lines up to about 200 MPa with great accuracy. For xenon and krypton there were no previous data. Analysis of lattice parameter changes of solid argon and krypton yielded values of (dP/dT) over a range of about 5% of the molar volume within the respective triple points, of precision at least five times better than previous values.

An outstanding question has been the probable role of many-body intermolecular forces in solid noble gases. In these solids such forces should be relatively large and therefore most accessible to study. Many published studies have been consistent with a rather small role in the heavier gases, but, on the other hand, no direct refutation has appeared of the direct--and sensitive test, in principle--of measuring the vacancy free energy in krypton and comparing it with the cohesive energy per atom, which was published by Losee from this project 10 years ago. This indicated a considerable magnitude of the effect in krypton. Subsequent work, while consistent with small effects, has often contained circular ("self-consistent") arguments. Return to this question, by our quasi-isochoric technique of measuring thermal vacancy content, (i) has confirmed the project work of Schwalbe (published 1977) on argon, which has vacancy energy near the cohesive energy, as expected, and (ii) has provided independent support for the unusual results of Losee on krypton, as was the question. Moreover, this work, by Macrander, is of precision sufficient to establish the free volume of thermal vacancy formation in krypton, hitherto unavailable experimentally. The question has been pointed, not blunted, by these developments.

Other Results: The first direct measurement of thermal vacancy concentrations in hcp ⁴He have been made. From this direct information, by scaling arguments (because no self-diffusion data exist), it appears that self-diffusion in hcp ⁴He is by thermal activation over a barrier.

Because success of the program depends upon understanding and control of the crystal growth process in simple molecular crystals, this has been analyzed for solid methanes and for several crystals bcc ³He, hcp ⁴He, and hcp ³He. The heliums form a particularly attractive system for such studies because the physical parameters governing growth can be varied over wide ranges in one chemical species. Once again in 1977, as at a previous International Conference on Crystal Growth in Boston, the group reported on growth in materials at melting temperatures below 1/10 of the lowest temperature of any other group.

Instrumental capabilities of the program were considerably enhanced during the year, by the operation of our own "position sensitive" x-ray detector (which made the solid H_2 work possible) and by the rebuilding of our orientable x-ray diffractometer to make absolute measurements of lattice parameters. A position sensitive detector was also added to our workhorse back-reflection x-ray camera, in order to speed set-ups of very weak Bragg spots used in melting and P-V-T studies. Digital indication of angles was implemented for the diffractometer. A PDP-11 system now is in use for data acquisition with the millikelvin x-ray system. Pressure measurements of high sensitivity have been added to the helium crystal growth cells. Altogether, the group has unique capabilities for preparation and x-ray study of very weakly-scattering specimens, at pressures up to 200 MPa and temperatures down to 60 mK.

Results Expected FY79: Solid-solid phase transitions in CH_4 and CD_4 methanes will be followed if possible at moderate pressures, in order to establish good (dP/dT) values for the phase boundaries. Such information, which is not now available, is needed to test theoretical treatments, including forms of Landau theories and existing refinements including crystal field effects. The coexistence of crystalline phases in methanes, first observed by this group, and identified as analogous in some ways to classical phenomena occurring in quartz, bear further scrutiny to elucidate the nature of the molecular rotational disordering and the regions and sources of metastability of phases.

To provide more direct measures of the order parameters associated with the phase transitions, it may prove possible to measure elastic constants of the methanes near the phase transitions, by means of the pulsed Debye-Sears optical diffraction technique developed in the group some years ago. Attempts to do this will depend somewhat on the temperature ranges of success (or not) on methanes achieved in Stoicheff's Toronto groups using Brillouin scattering. Likely, the latter work will be limited to near melting, and our attempts should proceed. Conventional ultrasonic work elsewhere has not been successful.

The importance of vibrational contributions to the energy and entropy of a real quantum crystal containing thermal defects is not understood. Solid mixtures of 3He in 4He will be used to measure vacancy content in 4He -rich bcc phases (pure 4He has too limited a bcc temperature range available). Two complementary tools are available as strong probes of vibrational content: isotopic mass change (30%) and volume compression (about 15% achievable). Existing and continuing NMR data on the mixtures (work done at Sussex, at Orsay, and at Kharkov) indicate several species of mobile structural defects. Some have wavelike character, i.e., exhibit q-dependent collective modes unusual for mobile defects. Determination of the thermal defect content should permit quantitative approach to the curiosities and anomalies of defect-defect scattering in this quantum system.

The necessity of in situ preparation and characterization of He and H₂ crystals has limited the rate of acquisition of data in the range down to 60 mK, where current technology, although strong, is not continuously reliable for x-ray scattering work. We propose to build another milli-degree diffraction cryostat, and put it into service. This will about double the world's capability for such x-ray work. (Incidentally, the success of our first machine, as described in Rev. Sci. Instrum., has encouraged ORNL scientists to consider a similar neutron-scattering cryostat.)

Probably the questions about (quadrupolar) spin glass behavior of H₂ (and D₂) will recede to temperatures below 150 mK and concentrations below 40% of J=0 spin species. As the debate develops, the group will arrange its hydrogen priorities appropriately.

Equation-of-state studies of simple solids can move into a new regime of critical confrontation between theory and experiment. Measurements of (dP/dT) in solid xenon at different densities will be attempted, along the lines of our successful work on argon and krypton. Monte-Carlo and molecular dynamics calculations, using what may be realistic potentials, are already underway at NRC Ottawa, for comparison purposes. Separate probing of the multibody potentials (e.g., triple-dipole and triple-overlap) by study of thermal vacancy concentrations in compressed xenon, where the effects are relatively largest (except for radon!) may be possible.

Results Expected FY80: Exciting prospects appear to be developing at ANL with the Intense Pulsed Neutron Source and associated instruments. Novelty of the source and of the proposed instruments precludes a detailed statement at this time of plans for use by this group. But several lines of possible investigation are under study. The possibilities are not being limited to systems of condensed gases, although some molecular systems showing orientational disorder appear attractive. The general aim would be choice of problems, within the DOE charter, upon which complementary x-ray and neutron-scattering probes of solid structures and excitations would be most effective. Crawford of ANL (formerly with this group) is the natural link for collaboration. He has particular responsibility in the area of IPNS instrumentation.

We hope, but perhaps cannot realistically expect, that the most prominent questions about defect structures and mobility in solid heliums will be settled during this time period. Helium has given surprises before! Quantum effects (i.e., cases where the momenta of the defect entities, in q-units, are comparable to interatomic distances) are remarkable examples of energy transfer and dissipation in solids which invite a deep search for understanding.

Relationship to Other Projects: Experimental studies of solid-solid phase transitions due to molecular reorientation and nuclear spin isomer conversion in solid hydrogens are proceeding at Harvard (Pound and students, NMR), at Kharkov (Krupskii and colleagues, PVT work), at KFA Jülich (Stiller and colleagues, neutron scattering), at CEA Saclay (Sullivan and colleagues, NMR). Other properties of solid hydrogens are of interest, and are being studied, for example at Duke (Meyer), at British Columbia (Hardy, microwaves), and Amsterdam (Silvera and colleagues). High-pressure (to 2 GPa) equation-of-state studies on isotopic hydrogens and mixtures are proceeding at Los Alamos (Mills, Grilly). None of the above work is of a structural nature below 1 K, where the greatest unresolved questions lie, and where work on the present project is concerned.

Current theoretical work includes microscopic work, for example: (Harris, Pen; Berlinsky, British Columbia; Raich, Etters, Colorado State; Diederichs, Biem, Giessen). Phenomenological analysis from the Kurchatov Institute of Atomic Energy has recently been published (Geilikman and Ivantev).

Work on phase transitions and properties of solid methanes is not quite so extensive, but substantial current programs are proceeding at McMaster (Morrison and students, neutron scattering), KFA Jülich (Press and Hüller, neutron scattering work and theory), Kyoto (Yamamoto and colleagues), Toronto (Stoicheff and students, Brillouin scattering), as well as individual smaller efforts at LBL, Tokyo, etc. None of the above work is duplicated by the present project, which mostly employs high-precision x-ray diffractometry and thermal analytical techniques. It should be noted that methane rotational transitions are somewhat similar to those found for some ions in, for example ammonium halides (Garland, MIT), CBr_4 (Dolling, Chalk River) KCN and KCN/KBr (Rush, Rowe, NBS), NaOH (Dach, Hahn-Meitner Inst.), etc.

Thermal expansion is a stringent overall test of anharmonic models for crystals, because it tests high-order derivatives of the crystal free energy. Few laboratories, besides this project, have produced work of the highest quality on condensed gases: Iowa State Ames Lab (Swenson) is one. A more microscopic probe is second-order Raman scattering, with some early work at Bell Labs (by Fleury), being less extensive than the "two-phonon" analysis of the present project. Thermal conductivity in compressed solid neon has been measured by Clemans and Klein here, in a project now concluded; analysis of such studies may be even more complex than for thermal expansion. Of course, one-phonon properties are the base upon which one analyzes these higher-order refinements in condensed gases. Past contributions came from BNL (Dkalyo and others, phonon dispersion), from Toronto and Newfoundland (Kieft and Clouder, Brillouin scattering), and Munich (Lüscher and coworkers, ultrasonics, stimulated Raman, neutron scattering), etc.

Studies of self-diffusion, atomic, or ionic transport in quantum crystals are presently carried out at the University of Massachusetts, Case-Western Reserve, Bell Laboratories, the University of Sussex (United Kingdom), CEA

Saclay (France), Institute of Physical Problems (Moscow), Kurchatov Institute for Atomic Energy (Moscow), the Physico-Technical Institute (Kharkov), and occasionally elsewhere. The speculative content of current theoretical formulations is presently large. There is a richness among this speculation, however, which encourages hope that some truly new phenomena will be identified and established.

In all of the above cases, while theoretical and experimental interest and activity exists at a high level in the national (and other) laboratories of a variety of countries, the work complements the present project but does not directly duplicate any part of it. This is no accident; active contact is maintained with all groups called current above.

Publications (Calendar Year 1977):

- B. A. Fraass, S. M. Heald, and R. O. Simmons
Growth of Several Quantum Crystals: CD_4 , ^4He , and ^3He
J. Crystal Growth 42, 370-375 (1977)
(Also presented at ICCG-5 Meeting, July 1977, Boston, MA)
- B. A. Fraass, S. M. Heald, and R. O. Simmons
Thermal Vacancies in Solid Helium
Proceedings of 1977 International Quantum Crystals Conference
J. R. Sites, Ed. (Ft. Collins, CO, 1977) pp. C73-77
- S. M. Heald and R. O. Simmons
Cryostat for Accurate X-Ray Diffractometry of Crystalline Helium
to 60 mK and 25 MPa
Rev. Sci. Instrum. 48, 316-319 (1977)
- A. T. Macrander and R. K. Crawford
Density of Solid Argon at Melting
Physica Status Solidi 43, 611-617 (1977)
- D. R. Baer, B. A. Fraass, D. H. Riehl, and R. O. Simmons
Lattice Parameters and Thermal Expansion of Solid CD_4
J. Chem. Phys. 68 (to be published)
- S. M. Heald, D. R. Baer, and R. O. Simmons
X-Ray Diffraction Study of Thermal Vacancies in Solid ^3He
Solid State Commun. (submitted to)
- R. K. Crawford, D. G. Bruns, D. A. Gallagher, and M. V. Klein
Raman Scattering from Condensed Argon
Phys. Rev. B (submitted to)
Also supported by National Science Foundation Grant DMR-76-01058

Theses (Calendar Year 1977):

- Albert Tiemen Macrander (R. O. Simmons, Advisor)
X-Ray Diffraction Study of Compressed Solid Argon and Krypton
Ph.D Thesis

Nuclear Magnetic Resonance in Solids

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Senior Staff: Charles P. Slichter, Professor
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 Stephen H. Couturie, Research Assistant
 Claus D. Makowka, Research Assistant
 Howard E. Rhodes, Research Assistant
 Serge Rudaz, Research Assistant

Object: Our general program consists of two components:

- 1) The use of magnetic resonance methods to study the microscopic aspects of materials with unusual physical properties. This work builds on our long experience in magnetic resonance which enables us to work on problems of unusual experimental difficulty.
- 2) Exploration of novel experimental methods (other than magnetic resonance). Our present work on measurements of electrical conductivity using a scanning electron beam is a current example.

In recent years, the power of magnetic resonance as an experimental technique has increased enormously. None of the experiments we do today were possible a few years ago. The prime reasons are: i) use of superconducting solenoids which make possible magnetic fields 5-10 times stronger. Our work on single-crystal dilute metal alloys would have been impossible without the extra sensitivity and the resolving power of such high fields. We could not resolve the structure on the Se resonance (described below) produced by the charge density waves without the solenoid. ii) Multi-channel digital averagers which permit one to improve signal to noise ratios by averaging for long periods. iii) Computer methods for calculating complex spectra (which enable one to make precise theoretical interpretations even when one must observe spectra smeared by such things as powder averages) and for processing data to improve signal to noise ratio. iv) Development of new resonance methods, such as various forms of double resonance and special pulse trains, which greatly increase sensitivity or permit observations of a weak resonance obscured by a strong one.

A. Magnetic Atoms in Non-Magnetic Metals. We have been studying two aspects of the problem of magnetic atoms in non-magnetic metals: (a) the Kondo effect, and (b) the general nature of the electronic structure of the magnetic atom. We are exploring embarking on a third aspect, the phenomenon of spin glasses.

A great deal is known about magnetic atoms in insulators. When these same atoms, for example atoms of the iron group in the periodic table, are put in metals, there is a strong interaction between the magnetic atom and the conduction electron, as a result of which two phenomena arise.

The first phenomenon is that the magnetic atom becomes a potent scatterer of electrons, especially at low temperatures. Theoretical treatment of this problem, first done by Kondo (hence the name "Kondo effect"), turns out to be a many body problem of exceedingly great difficulty. The development of renormalization techniques has recently led to significant advances. Experimental difficulties have also led to controversy over the true experimental facts. Our group has developed techniques which have clarified a great deal of the experimental uncertainty.

Most of the theoretical work has been based on an idealized picture in which the magnetic atom possessed only spin angular momentum. Schrieffer and Coqblin have shown that to explain the observed existence of a Kondo effect for Ce atoms in lanthanum or yttrium, one must take account of the orbital angular momentum. Such effects have not yet been included in treatments of the iron group atoms, but should be as one learns how to describe the atoms (see below).

The second phenomenon that conduction electrons produce is to make possible transfer of electrons from the magnetic atom to the conduction band, thus producing great uncertainty as to the effective ionic state of the magnetic atom, and the extent to which the internal couplings and energy level splittings differ from those of atoms in insulators. For example, how much does screening by conduction electrons affect the crystalline electric fields which play such a vital role in determining the magnetic character of these atoms in insulators. Our experiments are providing some of the first direct evidence as to the electronic structure of these atoms, comparable to the sorts of pictures one has of magnetic atoms in insulators.

The two problems are closely related since the level of theoretical understanding of the Kondo problem has now been pushed to the point that more realistic, less idealized models of the magnetic atom are now needed to test the theory. For example, what is the role of the orbit in the Kondo effect?

Our experiments consist of studying the nuclear resonance of Cu^{63} nuclei which are near neighbors to the iron group atom present in dilute alloys. The magnetic atom magnetizes the conduction electrons producing, so to speak, a cloud of magnetization surrounding the magnetic atom. Our experiments enable us to measure the magnetization density of this cloud at specific and known neighbor positions to the magnetic atom to make a map of the magnetization by use of metal single crystals. Theoretical techniques enable us to relate the magnetization density to the Kondo effect and the electronic structure of the magnetic atom. We can thus study the spatial form of the map and how the map changes with temperature.

Spin glasses represent still a third aspect of these dilute alloys, and are currently a topic of substantial theoretical and experimental activity at many places. The spin glass phenomenon manifests itself in experiments such as magnetic susceptibilities--as one cools one finds a cusp in the susceptibility versus temperature which occurs at a temperature which goes roughly as the concentration of magnetic ions to the two-thirds power. It is thought that the cusp signals a phase transition arising from the interaction between magnetic atoms. A theoretical description of the characteristics of the low temperature phase is a problem of great difficulty. P. W. Anderson received the Nobel Prize in Physics in part for his contributions to the theory. Various experimental methods have been employed to study the phenomenon. There are theoretical arguments that the phase transition should be studied in the absence of applied magnetic fields, but most magnetic measurements require the application of a static field. Utilizing some of our background in studying some of these alloys, we are exploring resonance methods of doing so.

B. Transition Metal Dichalcogenide Layer Compounds. The transition metal dichalcogenide layer compounds such as TaS_2 , TaSe_2 , and NbSe_2 possess remarkable properties. Consisting of planes of transition metals atoms sandwiched between planes of the dichalcogenide: 1) they are superconductors; 2) they can absorb large amounts of foreign molecules (easily doubling the number of atoms in a sample), a process called intercalation; 3) their superconducting transition temperature, T_c , is tunable by selection of the molecular species; 4) they exhibit charge density waves (CDW's), a remarkable state in a conductor in which the electron charge density possesses standing waves in contrast to its usual uniform density characteristic of most metals. We have carried out studies of intercalation with hydrogen.

We are currently studying the charge density wave by means of its effect on the nuclear magnetic resonance. Nuclear magnetic resonance can measure such things as the amplitude of the charge density wave at different temperatures and crystallographic location of the maximum charge density. We have a special interest in testing the theories related to the wavelength of the charge density wave which, over a certain temperature range, has the remarkable property of bearing no simple relationship to the periodicity of the crystal lattice. Our work on this latter topic is an outgrowth of the theoretical predictions of W. McMillan of our Physics Department, who has proposed interesting conjectures related to the wavelength.

C. Catalysis. Our work on dilute magnetic alloys has stimulated our interest in other areas of scientific and practical importance requiring high sensitivity. We are currently investigating potential problems in catalysis.

We have chosen an initial experiment which combines high interest with relatively low risk--the study of platinum catalysts, supported on alumina, on silica, or on mixtures of alumina-silica.

These catalysts, which are of great practical importance in the so-called reforming reactions with hydrocarbons, typically consist of small particles (10-50 Å diameter) of platinum, supported by the insulating alumina or silica. For such particles, a large fraction of the atoms are on the particle surface.

Although typically the platinum atoms are only a few percent of the atom numbers in the catalyst, we believe the fraction of atoms on the surface is sufficiently large that there is a good chance of seeing their resonance using the sensitive methods we have previously employed.

The resonance spectrum of platinum is expected to be fairly simple since, being a spin 1/2 nucleus, it does not experience electric quadrupole interactions. Its very large Knight shift of several percent should be different for surface atoms from those on the interior. Moreover, depending upon what crystal face forms a surface, the Knight shift might differ.

If we can find surface atom resonances, the way is then opened for observing changes in them when another atom is bonded at that site and, in fact, should depend upon what atom is bonded. There exists, then, a potential route to learn about the surface couplings to molecules involved in catalysis. There is also the possibility of exploring the resonances of atoms adsorbed on the surface.

The potential applications seem very large, but depend upon success of the first stages. Note that so little has ever been measured on such small particles that they are of major scientific interest quite apart from their role in catalysis.

We have observed platinum resonances in all of our samples, including samples provided through an interesting and fruitful interaction with Dr. John Sinfelt of Exxon, a well-known expert on catalysis.

D. Photovoltaic Devices--Deep Traps. There are a variety of semiconducting devices involving interaction of light with electric voltages and currents. Some of these devices use light to generate voltages, others use voltages to generate light. The former clearly are important as means of converting solar energy to electrical power. The latter are important because they provide very low energy light sources and because they are of potential use for integrated optics, an energy conserving communications technology.

An important problem area in all such devices is the nature and role of the so-called electronic deep traps. As a result of discussions with J. Dow of our department, we have been doing exploratory experimental and theoretical studies of a model system, mixed III-V compounds containing nitrogen, a system which is under intensive study at the University of Illinois. There are two experimental programs in other groups at Illinois, one led by N. Holonyak, the other by B. Streetman. The theoretical work is led by J. Dow. Mixed crystals of GaAs and GaP have the remarkable property that the nitrogen atom goes from being a shallow trap in pure GaP to being a deep trap for crystals containing approximately equal amounts of arsenic and phosphorus. We have been investigating the feasibility of a program to study the microscopic properties of these traps over a range of such mixed crystals in a set of experiments to obtain information both about the dynamics and the microscopic structure of the trap.

Results FY78:

Most Significant Accomplishments: 1) We have extended our calculations aimed at interpreting our experimental studies of dilute alloys of Cr, Mn, and Fe atoms in Cu to calculate the charge density of the 3d electrons as a function of distance from the nucleus within the magnetic atoms. We find that the shape of the charge density closely approximates that of the free atom, showing that there is good meaning to the concept of the number of 3d electrons on the atom and enabling us to determine the number of 3d electrons on the atom when it is in copper. Comparison of the charge density when the atom is in the metal to that of the free atom shows that even in the metal the number of 3d electrons is nearly integral: for Cr 4.2 ± 0.2 , for Mn 4.9 ± 0.2 , and for Fe 7.0 ± 0.2 .

The jump of 2 electrons in going from Mn to Fe, its neighbor in the periodic table, lends strong support to the general viewpoint of Hirst who has argued that the iron group atoms act much like ions in insulators, with a specific electron configuration (e.g., $3d^4$ for Cr, $3d^5$ for Mn, etc.), Russell-Saunders coupling, crystal field splittings, etc.

2) We have carried through a detailed analysis of the temperature dependence of the Knight shift of the Cu atoms which are neighbors to Cr and Fe atoms. Our measurements enable us to determine for the first time the temperature dependence of the spin susceptibility of the magnetic atom. As reported last year, our experiments show that Cr has a large temperature independent contribution to its spin susceptibility, in contrast to both Mn and Fe.

We have been able to explain both the qualitative and quantitative data on total susceptibility and the spin susceptibility in terms of Hirst's concepts (see above). These calculations give a very detailed picture of the electronic state of the Cr and Fe ions, and agree with the generally accepted picture of Mn. For example, for Cr, we conclude the atom has a spin of 2 which is coupled to the orbital angular momentum of a 3-fold degenerate orbital state to give a ground state with effective angular momentum, J, of 3. There are

two excited levels of $J=2$ and 1 respectively, split by the spin-orbit coupling. At liquid helium temperatures, only the $J=3$ state is occupied, but application of the magnetic field admixes the $J=1$ and 2 states, giving a temperature independent contribution to the spin susceptibility.

3) We have observed the effect of the charge density waves in a single crystal of $2H-TaSe_2$ by observing the splitting of the Se NMR produced by the charge density wave in the strong magnetic field of our superconducting solenoid. Since Se has a spin $1/2$, it does not have an electric quadrupole moment and experiences no direct electric interactions, but the Knight shift produces the splitting. By use of a superconductive solenoid, the Knight shift splitting (which is proportional to the strength of the magnetic field) can be made large enough to be observable. Efforts to observe the Ta NMR have been fruitless, as were our efforts to observe the splitting of the Se NMR in our ordinary iron-core electromagnets. We have observed three resolved lines at liquid He temperature, corresponding to the three non-equivalent Se nuclei in the commensurate charge density wave, and in the temperature regime where there is an incommensurate wave we have found a two peak resonance pattern similar to that predicted by Follstaedt and Slichter in their paper on charge density waves in potassium [Phys. Rev. B13, 1017 (1976)].

Other Results: 1) In the area of catalysis, we have carried out an analysis of the optimum size Pt particles for observation of the NMR of surface atoms. Working with that sample, we have found that the NMR of the Pt atoms not in the surfaces has a very different temperature dependence from that of Pt in micron size particles. We have calculated the approximate size of the Knight shift to be expected in surface atoms where the surface is clean and when the surface is coated. We have also calculated the width of the NMR line of the surface atoms. We have not found any surface atom resonances using the conventional iron magnets. Since one expects substantially improved sensitivity at high magnetic fields, we will make a search using the superconducting solenoid.

2) We have looked at the Ga and P resonances in pure GaP, and have characterized the resonances. We have looked unsuccessfully for the N resonance in GaN (though we have not searched using the superconducting solenoid) which makes us pessimistic that we can observe the N resonance as a dopant in GaP crystals.

We have made an analysis of combined optical-NMR experiments using N-doped GaP, but find that the short lifetime of the optically excited state makes it unlikely that we can maintain a high enough population of excited N traps to observe them directly.

Results Expected FY79:

A) Magnetic Atoms. We will investigate theoretical implications of our models for Cr and Fe atoms in Cu on the conduction electron spin transmission experiments of Schultz and Monod (CuCr) and Silsbee and Ritter on CuFe. The picture

we come to from our results differs from that postulated from electron spin results on CuCr , but we see a possible way in which we can reconcile the results. An important aspect of the theory is that we are now discussing these atoms in a very detailed manner. Both orbital and spin angular momenta contribute to the magnetic moment and are involved in the Kondo effect. Coqblin and Schrieffer have shown for Ce in lanthanum or yttrium that the existence of orbital angular momentum has a profound effect on the coupling of the atom to the conduction electrons. We will follow their approach in analyzing the implications of our picture of the atoms on the coupling of the atoms to the conduction electrons.

The dilute alloy samples we have been studying are the sort of systems which are spin glasses. Because of the importance of spin glasses and the present substantial theoretical interest in them, we have been examining theoretical questions which are of interest and possible experiments to answer these questions. We have several resonance experiments under analysis which would get at basic aspects of spin glasses. One, for example, might shed light on the static and dynamic properties of the local field. Whether or not any of the experiments will be feasible cannot as yet be decided. We have begun work on testing the experimental feasibility of a concept to study the local fields in the absence of an applied laboratory field, the situation most desired from the theoretical point of view.

B) Transition Metal Dichalcogenide Layer Compounds. We will refine our observations of the effect of charge density waves on the Se NMR in 2H-TaSe_2 and carry out a theoretical interpretation of the data. Since the temperature of the incommensurate to commensurate transition is sample dependent, we need to make an independent measurement for our single crystal. Given precise knowledge of the transition temperature, we hope the data will enable us to test the validity of McMillan's concept of "discommensurations". We expect to be able to determine the temperature dependence of the amplitude of the charge density wave in both the commensurate and incommensurate phases.

C) Catalysis. We will study our present Pt sample to try to understand why its line-width and spin-lattice relaxation are so different from those of Pt samples with micron size particles. We will look for the resonance of surface atoms using the much higher magnetic fields of the superconductive solenoid. Though we have not as yet detected surface atoms, we are strongly encouraged by the fact that on a sample with particles in the 50-200 Å size range, the Pt NMR of interior atoms seems so different from that in much larger size Pt particles.

We will initiate investigation of NMR of foreign atoms on the Pt surface to characterize the intensity and properties of the resonances so that we can analyze their use in NMR studies of the surface.

D) Photovoltaic Devices. We are currently evaluating the results to date to decide whether or not to proceed with further experiments. Work to date has made it clear that the concentrations of N necessary for NMR can only be obtained by growing the samples by vapor phase epitaxy. The samples are then only a few microns thick. We would need to stack a very large number to get adequate sensitivity. We have concluded that the lifetime of the N trap is too short for us to observe excited N directly.

Results Expected FY80:

A) Magnetic Atoms. We will focus on spin-glasses if the present experiments we have initiated are successful. If they are not, we will probably abandon this area.

B) Transition Metal Dichalcogenides. Probably our work in this area will be completed.

C) Catalysis. We will focus most heavily on study of the NMR of foreign atoms (probably H and C^{13}) on Pt surfaces, and will begin analysis of other catalytic systems.

D) Photovoltaic Devices. What we do will depend on our evaluation of the experiments we have nearly completed.

Relationship to Other Projects:

A. Dilute Alloys of Iron Group Atoms in Copper. At the Sandia Laboratories, Dr. Albert Narath and Dr. David Follstaedt (a recent Ph.D. from our group) have been studying extensively the nuclear resonance of the magnetic atoms themselves. Their work complements and supplements but does not duplicate our work on the copper atoms in the vicinity of the magnetic atom. We are in close communication with them and have in fact supplied them with samples which they have used in certain of their experiments.

B. Transition Metal Dichalcogenides. Our group initiated the work on these materials at the University of Illinois. We were able to do this because we had as a postdoctoral research scientist, Dr. Steven Meyer, who came from Stanford University where he worked with Professor Geballe, one of the pioneers on such materials. Our group has been a principal source of samples worked on by the others in the laboratory, notably M. Klein and his group who have studied Raman effects in these compounds. We have assisted F. C. Brown and his group in techniques of crystal growing.

At Ames Laboratory, Borsa, Torgeson, and Shanks have been studying the NMR of Se in $2H-TaSe_2$ and $2H-NbSe_2$, but they have been working with many oriented crystallites rather than a single crystal, and have not resolved the structure we have found in $TaSe_2$ by using a superconducting solenoid.

C. Small Particles of Platinum. These materials are widely studied as catalysts, but we believe the experiments we are undertaking on the nuclear resonance are unique.

D. Photovoltaic Materials. Our work is based upon samples supplied to us by other groups in the MRL and by the Coordinated Sciences Laboratory, University of Illinois (both supported by federal contracts). Theoretical stimulus from the work arises from the work of J. Dow of our department (supported by the National Science Foundation). There is widespread activity in other government laboratories and in industrial laboratories on the general class of photovoltaic materials but we believe the work we are investigating is unique.

Publications (Calendar Year 1977):

D. M. Follstaedt and C. P. Slichter
NMR Study of Copper with Vanadium Impurities
Phys. Rev. B16, 21-29 (1977)

D. C. Abbas, T. J. Aton, and C. P. Slichter
Ionic Model for Cr, Mn, and Fe Impurities in Cu
Proceedings 23rd Conf. on Magnetism and Magnetic Materials, Minnesota, 1977
(to be published in J. Appl. Phys.)

T. S. Stakelon and D. M. Follstaedt
Sensitivity Considerations for NMR in Metal Single Crystals
Rev. Sci. Instrum. (accepted for publication)

J. David Cohen and Charles P. Slichter
A Theory Relating NMR Satellite Data to the Structure of Iron Group
Impurities in Copper
Phys. Rev. Lett. (in press)
Also supported by National Science Foundation DMR-72-07661

J. David Cohen and C. P. Slichter
A Theory Relating NMR Satellite Data to the Electronic Structure of Iron
Group Atoms in Copper
Proceedings 23rd Conf. on Magnetism and Magnetic Materials, Minnesota, 1977
(to be published in J. Appl. Phys.)
Also supported by National Science Foundation DMR-72-07661

Theses (Calendar Year 1977):

Daniel Cornelius Abbas (C. P. Slichter, Advisor)
Ionic Model for Chromium, Manganese and Iron Impurities in Copper
Ph.D. Thesis

James Peter Long (C. P. Slichter, Advisor)
Scanning Electron Microscope Technique for Measuring Electrical
Conductivity: Application to Tetrathiafulvalene-Tetracyanoquinodimethane
Ph.D. Thesis

Physics of Refractory Materials

Principal Investigator: Wendell S. Williams, Ph.D.
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Object: The scope of this research program is the physics of selected ceramic materials, the transition metal carbides that have identifiable connection with presently envisioned energy technology. Although all six members of this class of compounds have similar refractory properties, there are individual differences that identify certain compounds as best suited for specific purposes. Hafnium carbide has the best spectral selectivity of any material for photo-thermal conversion; tungsten carbide is the best catalyst known for certain reactions under poisoning conditions; niobium carbide and tantalum carbide are good superconductors while the other carbides are not. Part of our goal within the scope of this program is to identify the details of the electronic structure that are responsible for the individual differences among members of this class. With such knowledge, further optimization of properties may be possible. We have studied, or are currently studying, thermal conductivity, electrical conductivity, order-disorder transformations, optical reflectivity, microhardness, dislocation velocity, yield stress, catalytic behavior, internal friction, microstructure, electron energy states and superconductivity.

The extraordinary ability of platinum to form H_2O from H_2 and O_2 is shared by tungsten carbide. This material is a substitute candidate for Pt in the oxidation of hydrogen in acid-electrolyte fuel cells. This project seeks to clarify the influence of suspected point defects--oxygen impurities and carbon vacancies--on the catalytic effectiveness of "WC". An electrochemical cell has been constructed and instrumented to measure hydrogen ion current in the electrolyte--an index of catalytic effectiveness, and electrodes of several transition-metal carbides--both powders and single crystals--are being fabricated. Nonstoichiometric, oxygen-doped cubic carbides will be tested in addition to defect hexagonal WC. The carbide electrode materials will be thoroughly characterized by AES, EDXA, SEM, TEM, X-ray, etc., and these findings correlated with the catalytic activity and recent theories of the relation between point defect electronic structure and hydrogen bonding to the defect site.

For efficient conversion of solar energy directly into usable heat, a receiver surface must have spectral selectivity, long-term stability and refractory character. Candidate materials are found in the class of refractory nonstoichiometric cubic carbides of the transition metals, e.g., TiC_x , HfC_x . This project seeks to make contact between measurements of the optical reflectivity of transition metal carbides and calculations of their electronic band structure.

Such basic knowledge can guide in the optimization of performance through exploitation of the several available experimental degrees of freedom: variation of carbon/metal ratio, x ; partial substitution of another transition metal; and partial substitution of nitrogen for carbon.

Of the several methods available for calculating electron energy states of solids, the Hartree-Fock method has been particularly successful for simple closed-shell-systems. This project attempts to extend the method to more complex solids--e.g., VO and CoO--and eventually to systems with partial overlap--e.g., TiC. A several-atom cluster approach shows promise for modelling the interactions of a surface with a gas and for determining the influence of point defects on surface properties.

The relation between the superconducting transition temperature, T_c , and several structural and compositional variables in the transition-metal carbide system is under investigation. These materials are B1 structure nonstoichiometric compounds, MC_x , where M is a transition metal of column IVB, or VB, of the periodic tables, and x is the carbon-metal ratio, varying between 0.5 and 0.97. Specially prepared powders of NbC_x with 5 selected values of x have been obtained. Their values of T_c will be determined. For a case of particular interest, $x = 0.833$, a long annealing treatment at 1020°C will be performed on the powder of that composition to induce the formation of the corresponding ordered phase, Nb_6C_5 . Measurements on its T_c , never performed before, will be made and the values compared with that for the disordered phase having the same composition. Any differences will be analyzed in terms of current interest in the influence of phase instabilities and soft phonon modes on superconducting behavior.

Results FY78:

Most Significant Accomplishments: 1) The unrestricted Hartree-Fock (UHF) model has been used to calculate the electronic properties of various clusters of atoms. Chemisorption, as well as other properties of interest, tends to be a localized phenomena. A small cluster of atoms can be used to simulate the solid for these studies. The problems of properly modeling a solid's bulk, surface, and corner have been resolved. In the case of ionic solids, the cluster is placed in a potential which simulates the electrostatic potential due to the rest of the solid. This approach necessitates writing a computer program that generates the Madelung potential at arbitrary points in two- and three-dimensional lattices, using a method due to Ewald and Posi. In the process, it was discovered that some of the published values for the perfect surface Madelung constants are incorrect. Corrected values were obtained and the implication of these corrections for understanding surface properties were explored.

2) Cobalt oxide, CoO, is being studied as a prototypical ionic transition metal compound. The bulk solid has been modeled by a CoO_6^{-10} cluster, and the model's calculated electronic structure compares well with the restricted Hartree-Fock bands for CoO. As well as indicating the lack of the p-d electron

interaction, the model calculation has suggested that there is significant spin polarization.

3) The (100) surface of CoO was studied computationally with respect to possible chemisorptive properties using a hydrogen atom as a prototypical adsorbate. For the study of the properties of a cobalt atom and vacancies in the surface, CoO_5^{-8} and O_5^{-10} clusters were used. Similarly, for an oxygen atom and vacancy in the surface, CoO and Co_5^{+10} clusters were used. The results indicate that the electronic structure is basically unchanged from that of the bulk and that the CoO + H potential surface curves are repulsive. The O_5^{-9} cluster is 2.57 eV lower in energy than the O_5^{-10} cluster and 1.25 eV lower than the O_5^{-8} cluster. These results suggest the possibility of an O^{-1} radical on the cobalt-defective surface which would be chemically active.

Other Results: 1) Results transmitted by B. O. Seraphin on optical reflectivity of the carbides at a 1000°C confirmed our earlier conjecture that the curves would be temperature insensitive in view of the prominent electronic-defect scattering.

2) In the WC catalysis study, the preparation of hydrophobic gas-diffusion electrodes is in progress. Discs of backing carbon paper have been wet-proofed by application of 30% PTSE dispersion in water. The filter apparatus has been modified for leak-less operation under partial vacuum to allow known loading of catalysts on the substrate paper. A series of titanium-carbide powders with a range of carbon-metal ratios from .6 to .97 has been obtained. An ultra pure water apparatus was set up for production of water to dilute concentrated ultra pure sulfuric acid for use as electrolyte.

3) Powders of niobium carbide have been received and initial measurements of superconducting transition temperatures have been carried out. The transition region is broad covering several degrees. Further homogenization of the specimen may be required.

Results Expected FY79: 1) Measurements of the superconducting transition temperature, T_c , for powders and crystals of niobium carbide will be completed. The dependence of T_c on x in NbC_x will be determined and compared with the literature. Specimens of $\text{NbC}_{.83}$ and Nb_6C_5 , having the same chemistry but different crystal symmetries and degree of order, will be compared.

2) Current-voltage Curves for carbide electrodes in acid electrolytes will be obtained. The catalytic performance of "WC" will be compared with that of TiC_x and NbC_x , and the dependence of currents on x will be determined.

3) Theoretical studies of carbides should lead to further understanding of H bonding to defect surfaces and of the electron energy band structure.

4) Samples of crystals with various values of the carbon-metal ratio will be provided to groups working on optical reflectivity. The dependence of reflectivity on x in TiC_x will be established.

Results Expected FY80: 1) The superconductivity results for NbC_x will be analyzed in terms of current theories of the dependence of T_c on details of the electronic structure, the role of soft modes, and order-disorder transformations.

2) The electrocatalysis results for WC, TiC_x , NbC_x , will be analyzed to resolve the question of the relative importance of band structure effects and local defects as sites for catalytic processes. Theoretical results on H bonding to carbide and oxide clusters including vacancies will provide insight for the interpretation of the experiments.

3) The dependence of the optical constants of TiC_x on the value of x will be reviewed and interpreted qualitatively by reference to earlier band structure and cluster calculations to provide information for the development of solar photothermal surfaces.

Relationship to Other Projects: A newly launched project, superconductivity in ordered and disordered niobium carbide, is being conducted in collaboration with C. B. Satterthwaite (Physics Department) as part of a joint investigation of superconductivity in nonstoichiometric compounds having V1 structure. His project has NSF support.

Our catalysis efforts are related to those of G. P. Wirtz (Ceramic Engineering) who is studying the catalytic behavior of oxides with MRL/DOE support.

The Hartree-Fock calculations of electron energy states in solids are being done in collaboration with A. B. Kunz (who is supported in the MRL by NSF).

Spectral selectivity in the carbides is under study jointly by this group and B. O. Seraphin (at the University of Arizona) and D. Lynch (of the Iowa State DOE Laboratory).

The Solid State Division of ORNL has become interested in the properties of transition metal carbides and has interacted with our group. This Division and the Metals and Ceramics Divisions of ORNL are proposing to establish a high-temperature materials laboratory and have invited the writer to sit on their Advisory Committee.

The Air Force Materials Laboratory, Dayton, Ohio, recently held a workshop to review earlier research on mechanical properties of the transition metal carbides with the aim of developing new turbine blade materials. The writer was an invited speaker.

A project on plastic deformation of carbide crystals was recently initiated at Cornell under DOE support. The principal investigator there, D. Kohlstedt, is a former student of the writer and cooperation with him will be continued.

Within the University of Illinois MRL, a recent study was conducted by M. V. Klein (Physics) on Raman scattering in the carbides, with crystals and consultation provided by our group.

During academic year 1977-78, the writer is serving as Head, Metallurgy and Materials Section, Division of Materials Research, National Science Foundation, Washington, D.C., on leave from the University of Illinois.

Publications (Calendar Year 1977):

J. Bethin and Wendell S. Williams
Ambipolar Diffusion Contribution to High-Temperature Thermal Conductivity of Titanium Carbide
J. Am. Ceram. Soc. 60, 424-427 (1977)

Dwight R. Jennison
Lithium Local-Orbital Energy Bands Using Kohn-Sham and Near Hartree-Fock Exchange
Phys. Rev. B 16, 5147-5152 (1977)

Dwight R. Jennison and A. Barry Kunz
Significant Differences Between Hartree-Fock and Local Exchange Energy Bands for TiO
Phys. Rev. Lett. 39, 418-421 (1977)
Also supported by National Science Foundation Grant DMR-76-01058

J. G. Baldoni and Wendell S. Williams
Deformation of Cemented Carbides: Initial Studies and Microstructural Analysis
J. Am. Ceram. Soc. (submitted to)

Wendell S. Williams, Marvin W. Johnson, and David Gross
Ceramic Models for Study of Piezoelectricity in Biological Solids: Part II
J. Am. Ceram. Soc. (submitted to)

Gerald B. Yost and Wendell S. Williams
Chemomechanical Effect in Doped and Intrinsic Silicon
J. Am. Ceram. Soc. (accepted for publication)

Gerald B. Yost and Wendell S. Williams
Load-Independent Microhardness of Brittle Solids
J. Am. Ceram. Soc. (submitted to)

A. Barry Kunz and David L. Klein
Unrestricted-Hartree-Fock Approach to Cluster Calculations II: Interaction of Cluster and Environment
Phys. Rev. B (submitted to)
Also supported by National Science Foundation Grant DMR-76-01058 and U. S. Air Force Grant AFOSR-76-2989

M. V. Klein, J. A. Holy, and W. S. Williams
Raman Scattering Induced by Carbon Vacancies in TiC_x
Phys. Rev. (accepted for publication)
Supported by National Science Foundation Grant DMR-76-01058

Theses (Calendar Year 1977):

M. W. Johnson (W. S. Williams, Adviser)
The Electromechanical Effect in Bone
Ph.D. Thesis

G. H. Yost (W. S. Williams, Adviser)
Microhardness of Hard Materials: Dependence on Load, Electrostatic Potential
and Chemical Environment
M.S. Thesis

AK-01-02-02-4 Particle-Solid InteractionsRadiation Damage in Solids

Principal Investigator: James S. Koehler, Ph.D.
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Supporting Agency: U. S. Department of Energy

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James E. Watson, Research Assistant

Object:

A. Hexagonal Metals. We are electron irradiating pure magnesium, zinc and cadmium at 1.8 K and measuring their recovery by using electrical resistance measurements during isochronal annealing. In cadmium, a new annealing peak is observed at 2.2 K. We are, at present, determining the shape of the resistance versus electron fluence to decide if long range interstitial migration occurs below 2 K in cadmium. (Abstract by M. Menendez and J. Koehler at March 1978 Physical Society Meeting.)

B. X-Ray Generation by Channeled Electrons. Our calculations suggest that well-channeled electrons in heavy metal single crystals should generate large numbers of short-wave length x-rays. A first attempt to observe the x-rays failed. We are improving our apparatus and plan to try again.

C. Defects in Silicon. P type silicon was electron irradiated at 20 K and the anomalous x-ray transmission (220 reflection) showed a 3% decrease upon irradiation. On annealing to 120 K, the transmission decreased another 1%, and on warming to 200 K it decreased another 2%. Since interstitials are known to be mobile at 20 K, we believe that these changes result from the presence of lattice vacancies which migrate in p type silicon at 180 K. A paper has been written and will be published (G. Fritsch and J. Koehler).

D. Tensile Deformation of Metal Multilayers. Hilliard and coworkers at Northwestern University have done tensile deformation experiments on alternating layers of gold, nickel and copper palladium. The individual layers ranged from 1×10^{-7} cm to 7×10^{-7} cm in thickness. They found an abnormally large initial slope of their stress strain curve which they interpret as an abnormally large elastic modulus. We believe that their measurements give valuable information about the interface between the two materials. A paper is being written. (See abstract at the March 1978 Physical Society Meeting, J. Koehler.)

Relevance to DOE. Since silicon is used for solar cells and electrical devices, information about defects in silicon is certainly valuable to DOE. The nature of the defects involved in self-diffusion in silicon is not yet understood.

The behavior of materials in nuclear and in fusion reactors is important to DOE. At present, defects in hexagonal and bcc metals are not understood.

The strength and the elastic behavior of layered materials constitute valuable information for a large number of applications. Hence, layered materials should be understood.

Results FY78:

Most Significant Accomplishments: In my opinion, the understanding that interface behavior contributes in an important way to the tensile properties of multiple layered structures was our most important research. This is important because it enables us to design materials having desired mechanical properties.

Other Results: The finding that vacancies and vacancy clusters in silicon produce measurable changes in anomalous x-ray transmission means that vacancies produce asymmetric lattice strains. Therefore, they can be studied more easily.

Expected Results FY79:

A. Body Centered Metals. We are installing a squid voltmeter in a low temperature cryostat. The ERDA Laboratory at Ames has supplied us with several pure samples of niobium and vanadium. These are of large diameter (1/16") so that usual resistance measurements are not sufficiently sensitive. We believe the squid will enable us to increase the sensitivity of our resistance measurements by a factor of about 4×10^3 . We will first determine the purity of the Ames specimens. If they are pure, low temperature electron irradiation and annealing experiments will then be done.

Expected Results FY80:

A. Melting. We have started calculations aimed at finding the nature of the elementary excitations which are important in liquids. We believe that the important excitations consist of the rotations of groups of atoms. Initially we tried to calculate the rotation of a ring of three atoms in solid argon using a two body interatomic potential valid at all separations. This required too large an energy. We, therefore, examined rotation of a ring of two atoms next to a lattice vacancy. This requires about 0.13 eV which is about correct for argon. The result suggests that melting nucleates at lattice vacancies, the surface, at grain boundaries or at dislocations. Melting then spreads throughout the solid. We intend to study the spreading. A paper is being written (Kozlowski and Koehler).

We are planning a coating experiment. A dislocation free germanium single crystal about 1 cm square by 0.1 cm thick is coated with a 2 micron thick epitaxial layer of GaAs. The lattice parameters of GaAs and Ge differ by only 0.124%. The melting temperatures of Ge and GaAs are 934°C and 1237.5°C respectively. Suppose the coated specimen is held at 984°C, then melting cannot nucleate at the outer GaAs surface. It may nucleate at the interface

between GaAs and Ge. We plan to try the experiment. Initially, we will simply observe the sample at high temperature optically, looking for shape changes. Note that this experiment does not prove or disprove that vacancies are required for nucleation. It tries to decide whether dislocations and external surfaces are required for nucleation.

B. Electron Scattering. The University of Illinois has recently purchased an electron microscope with an energy analyzer for the exit beam. This device enables one to do elastic electron scattering experiments. The energy resolution is 1.5 eV in 100 keV. We plan to use the device to study the geometrical structure of small vacancy clusters in quenched gold. A second problem would be to study age hardening in a quenched aluminum silver alloy. The energy analyzer would enable one to discriminate against plasma losses. We need to examine intensity problem carefully

C. We are attempting to use a two-dimensional Frenkel-Kontorova model to study both equilibrium defect geometry and also the dynamics of both perfect and imperfect two-dimensional crystals. Such calculations will be useful for phase changes, defect structure and migration energy calculations, and for defect resonance mode calculations.

Relationship to Other Projects: Our research benefits from the research done by the various low temperature research groups at the University of Illinois. In addition, we have profited by learning about particle detection from the nuclear research groups at Illinois. In addition, the Ames ERDA Laboratory is supplying us with pure bcc metals.

Publications (Calendar Year 1977):

J. S. Koehler
The Crowdion Using the Frenkel Kontorova Model
Phys. Rev. B (submitted to)

Theses (Calendar Year 1977):

None

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PUBLICATIONS

(Calendar Year 1977)

There were 62 DOE-supported publications for the Calendar Year 1977. In addition, there were 47 papers in process of publication.

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- A. Barry Kunz and David L. Klein, "Unrestricted-Hartree-Fock Approach to Cluster Calculations II: Interaction of Cluster and Environment," *Phys. Rev. B* (submitted to). Also supported by National Science Foundation DMR 76-01058 and U.S. Air Force AFOSR-76-2989.
- D. S. Matsumoto, C. L. Reynolds, Jr., and A. C. Anderson, "Localized Low-Energy Excitations in Two Polymers," *Phys. Rev. Lett.* (submitted to). Also supported by National Science Foundation DMR 77-08599.
- T. L. Smith, P. Anthony, and A. C. Anderson, "Density of Low Energy Excitations in Neutron Irradiated Vitreous Silica," *Phys. Rev.* (submitted to). Also supported by National Science Foundation DMR 77-08599.

AK-01-02-02-4 Particle-Solid Interactions

- J. S. Koehler, "The Crowdion Using the Frenkel Kontorova Model," *Phys. Rev. B* (submitted to)

Ph.D. DISSERTATIONS

(Calendar Year 1977)

Eighteen Ph.D. theses were completed and degrees granted with DOE support for the Calendar Year 1977:

ABBAS, D. C. Ionic model for chromium, manganese and iron impurities in copper. Ph.D. thesis, Department of Physics, C. P. Slichter, adviser.

ALLEN, P. C. Effect of pressure on ionic conductivity in rubidium silver iodide and silver iodide. Ph.D. thesis, Department of Physics, D. Lazarus, adviser.

BEAVERS, J. A. Stress corrosion cracking of Admiralty Metals in aqueous ammonia. Ph.D. thesis, Department of Metallurgy and Mining Engineering, E. N. Pugh, adviser.

BHOWAL, P. R. Deformation substructure and slip systems in directionally solidified $\text{Ni}_3\text{Al}(\gamma^1)\text{-Ni}_3\text{Nb}(\delta)$ eutectic composite to 600°C . Ph.D. thesis, Department of Metallurgy and Mining Engineering, M. Metzger, adviser.

CANTOR, D. M. A fully automated system for pulsed NMR measurements. Ph.D. thesis, Department of Chemistry, J. Jonas, adviser.

HOCKERT, E. N. Effects of high pressure on the photochromism and thermochromism of the anils. Ph.D. thesis, Department of Chemical Engineering, H. G. Drickamer, adviser.

HOOK, J. W. III. High pressure luminescence studies. Ph.D. thesis, Department of Chemistry, H. G. Drickamer, adviser.

HOUSE, G. L. Effects of high pressure on the luminescence properties of zinc sulfide phosphors. Ph.D. thesis, Department of Chemical Engineering, H. G. Drickamer, adviser.

ISAAC, R. D. Thermally activated dislocation motion including inertial effects in solid solutions. Ph.D. thesis, Department of Physics, A. V. Granato, adviser.

JOHNSON, M. W. The electromechanical effect in bone. Ph.D. thesis, Department of Physics, W. S. Williams, adviser.

KLICK, D. I. Luminescent decay and spectra of impurity-activated alkali halides under high pressure. Ph.D. thesis, Department of Physics, H. G. Drickamer, adviser.

LONG, J. P. Scanning electron microscope technique for measuring electrical conductivity: application to tetrathiafulvalene-tetracyanoquinodimethane. Ph.D. thesis, Department of Physics, C. P. Slichter, adviser.

- MACRANDER, A. T. X-ray diffraction study of compressed solid argon and krypton. Ph.D. thesis, Department of Physics, R. O. Simmons, adviser.
- PARK, S. M. Liquid phase sintering of heterophasic dielectrics in the system $\text{BaTiO}_3\text{-Pb}_5\text{Ge}_3\text{O}_{11}$. Ph.D. thesis, Department of Ceramic Engineering, D. A. Payne, adviser.
- STECKEL, G. L. Thermodynamics of oxygen in solid solution in vanadium and niobium-vanadium alloys. Ph.D. thesis, Department of Metallurgy and Mining Engineering, C. J. Altstetter, adviser.
- THOMASSON, J. W. Electromagnetic penetration depth in superconducting alloys containing magnetic impurities. Ph.D. thesis, Department of Physics, D. M. Ginsberg, adviser.
- TYNER, C. E. Effects of high pressure on thermal quenching of luminescence. Ph.D. thesis, Department of Chemical Engineering, H. G. Drickamer, adviser.
- YU, C. J. Electrical properties of thallic oxide single crystals annealed in oxygen. Ph.D. thesis, Department of Ceramic Engineering, G. P. Wirtz, adviser.

M.S. DISSERTATIONS

- BEGGS, D. V. Carbide formation at high temperature in vanadium-titanium-carbon alloys. M.S. thesis, Department of Metallurgy and Mining Engineering, C. A. Wert, adviser.
- BRUEMMER, S. M. High temperature precipitation in vanadium-titanium-carbon alloys. M.S. thesis, Department of Metallurgy and Mining Engineering, C. A. Wert, adviser.
- CHRYSSOMALLIS, G. The effect of pressure on the polarization of organic molecules in solution. M.S. thesis, Department of Chemical Engineering, H. G. Drickamer, adviser.
- FAY, R. M. Preparation and properties of bismuth tungstate. M.S. thesis, Department of Ceramic Engineering, D. A. Payne, adviser.
- FUJITA, J. Martensite-martensite transformations in Cu 39.8 at.% Zn and crystal structure. M.S. thesis, Department of Metallurgy and Mining Engineering, C. M. Wayman, adviser.
- YOST, G. H. Microhardness of hard materials: dependence on load, electrostatic potential and chemical environment. M.S. thesis, Department of Ceramic Engineering, W. S. Williams, adviser.