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MASTER

THE SCIENCE OF MATERIALS

Progress Report

January 1, 1979 - December 31, 1979

MATERIALS RESEARCH LABORATORY
UNIVERSITY OF ILLINOIS at URBANA-CHAMPAIGN

Prepared for
U. S. DEPARTMENT OF ENERGY
UNDER CONTRACT NO. DE-AC02-76ER01198

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ABSTRACT

This Progress Report contains a description of the research results of U.S. Department of Energy Contract DE-AC02-76ER01198 during the period January 1, 1979 through December 31, 1979.

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

The research program includes studies of the microchemistry, microstructure, deformation, corrosion and fracture of metals, ceramics and alloy materials, of the hydrogen embrittlement of metals, the mechanism of heat transfer across interfacts, 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 molecular interactions and bonding, on ionic conduction, phase transitions and radiation damage. Ferro- and pyro-electric materials with potential for solar energy applications are under development. The study of optical properties includes the mechanism of luminescence, the design of molecular photoreceptors, and new semiconductor materials for photovoltaic devices. The electronic properties of crystals are the subject of a continued effort to resolve current problems of transport and 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 at the University of Illinois Urbana campus is an interdepartmental unit of the College of Engineering. It is organized to facilitate interdisciplinary research into the properties of materials. The MRL is affiliated with the School of Chemical Sciences and the Departments of Ceramic Engineering, Electrical Engineering, Geology, Metallurgical and Mining Engineering and Physics. Primary support for the Laboratory has been derived from Contract DE-AC02-76ER01198 with the U.S. Department of Energy, Grant DMR-77-23999 from the National Science Foundation, and funds provided by the University of Illinois. The Laboratory maintains strong cooperative relationships with the Coordinated Sciences Laboratory, the Materials Engineering-- Mechanical Properties group and the contributing departments of the University.

The Department of Energy Program funded through the MRL preserves desirable features of both the DOE Laboratory Program and the DOE Universities Program. The block funds allow the development and maintenance of major central facilities through which expensive equipment serves multiple users. This method of funding also offers flexibility through local management in a way that is not ordinarily possible in the Universities Program. The size of the materials research community (about 25% of DOE funded) allows projects to be selected from a wide variety of areas and personnel. The MRL also allows research projects to be compatible with the university environment while coupled in an unusually effective way to long range DOE goals. In this mode of research, the individual projects function like those in the Universities Program but with the advantages of major facilities, program continuity and the community focus provided by the Laboratory. No faculty academic year salaries are supported by the agency funds; these resources are expended on research and the support of student, postdoctoral and technical personnel.

Two main faculty committees provide the Laboratory Director with technical advice and interface the MRL to the contributing departments. These are the Program Committee and the Departmental Liaison Committee. The FY 1979 Program Committee membership is: Professor H. K. Birnbaum (Metallurgy), Professor F. C. Brown (Physics), Professor H. G. Drickamer (Chemistry), Professor G. Ehrlich (Metallurgy), Professor W. L. McMillan (Physics) and Professor C. P. Flynn (MRL Director). The charge of the Program Committee is to provide technical advice on all aspects of the MRL research work. The Committee conducts a formal review of the individual Laboratory projects, operating in a three-year cycle. The Liaison Committee comprises the heads of the major contributing academic units, namely: Professor C. G. Bergeron (Ceramics), Professor H. S. Gutowsky (Chemistry), Professor R. O. Simmons (Physics), Professor G. W. Swenson (Electrical Engineering), Professor C. A. Wert (Metallurgy), and Professor C. P. Flynn (MRL). Its concerns lie with the new and visiting faculty, the overall health of the campus materials research community, and other personnel matters.

The same MRL administrative structure distributes local and NSF block funds for project research. The NSF and DOE programs are entirely separate but major benefits accrue to both from the sharing of research facilities and expertise.

In basic structure, the Department of Energy Program has two parts of approximately equal size. One is the solid state sciences component containing projects in solid state chemistry and physics. Its principal role is to perform fundamental research into the properties of materials, and to develop and maintain state-of-the-art experimental and theoretical capabilities in the solid state sciences. The second component is basic materials research, directed mainly by faculty with expertise in metallurgy and ceramics. These latter projects focus on basic research problems at the interface between materials science and major technological needs. A principal goal of the Laboratory is to link research in the solid state sciences with technological problems, through the interaction between the two components of the research program. These important interactions are not management-defined for the main part. They arise from a commonality of faculty interest, through the focus provided by the Laboratory.

Although in no sense programmatic, a number of areas of interdisciplinary effort exist throughout the Laboratory program. The focus of work on hydrogen in metals, for example, is one part of a larger interest in the behavior of light interstitials in metals. This involves eleven faculty in all (Professors Altstetter, Anderson, Birnbaum, Flynn, Fraser, Ginsberg, Granato, Klein, Rowland, Wert and Zabel). Quantum defect processes at low temperature are under similarly active investigation by Professors Anderson, Birnbaum, Granato, Holder, Koehler, Stapleton, and Simmons. This work is exploring a variety of intrinsic, impurity and irradiation-induced defect mobility processes at low temperature in metals, ceramics and molecular solids. There is a strong focus of expertise on the effects of high pressure on materials properties. Pressures up to 200 kbars and temperatures ranging from 1 to 1400 K are employed in these investigations. The contributing faculty include Professors Drickamer, Jonas, Lazarus, and Simmons. Other cross-disciplinary centers of effort lie in the areas of glassy materials, corrosion and cracking. These areas of common interest provide efficient avenues for the interaction of techniques and expertise in solid state sciences with materials problems ordinarily generated in the materials science community. The opportunity to fabricate novel materials configurations and characterize them using powerful microanalytical tools is being exploited in many areas of the materials sciences program.

A major resource of the materials program is provided by the MRL central facilities. Capital equipment housed in the facilities is accessible to all qualified users on the Urbana campus and is of special value to new young faculty in the formulation of their research plans. The MRL employs expert, research-level technical personnel to maintain the facility equipment and to instruct new users. It is the combination of university environment and opportunity for individual research that allows MRL to compete with industrial and other research organizations for these valuable personnel. The main materials-oriented facilities in the MRL are the Microstructure Facility and the Chemical Analytical Facility, currently being organized into a single Center for Materials Microanalysis, and the Materials Preparation Facilities. The facilities are more extensive than the DOE program funds alone permit, with additional support derived from NSF and University of Illinois funds. The operation of these central MRL facilities benefits the entire materials community on campus and, to an increasing extent, off-campus research workers also. At present, plans are in preparation to make the Microanalysis Center serve particular needs of the off-campus DOE Materials Sciences Program.

PROJECT TITLES AND PRINCIPAL INVESTIGATORS

METALLURGY AND CERAMICS

KC-02-01-01 Structure of Materials

Localized Corrosion of Passive Metals

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

Semiconductor Crystal Growth by Ion Beam Sputtering

J. E. Greene, Ph.D., Professor of Mechanical Engineering

Microchemistry of Solids

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

Theory of Polymers

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

Dynamic Structure of Materials Under Extreme Conditions of Temperature and Pressure

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

KC-02-01-02 Mechanical Properties

Hydrogen Behavior in BCC Metals

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

Mechanical Properties of Solids

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

Council on Materials Science

Robert J. Maurer, Ph.D., Professor of Physics

KC-02-01-03 Physical Properties

Interstitial Solid Solutions

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

Devitrification Behavior in Metal-Containing Silicate and Borosilicate Glasses

Haydn H. Chen, Ph.D., Assistant Professor of Metallurgy and Mining

Dielectric Solids

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

Structure, Cracking and Chemistry of Ceramic Grain/Boundaries and Phase Boundaries

William T. Petusky, Ph.D., Assistant Professor of Ceramic Engineering
Sherman D. Brown, Ph.D., Professor of Ceramic Engineering

Grain Growth in Alumina

David S. Phillips, Ph.D., Assistant Professor of Metallurgy and Mining

Hydrogen Trapping in BCC Refractory Alloys

Theodore J. Rowland, Ph.D., Professor of Physical Metallurgy

Studies of Disordered Materials in Electron Paramagnetic Resonance

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

SOLID STATE PHYSICS

KC-02-02-02 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

Exciton Collection from Antenna Systems into Accessible Traps

Larry R. Faulkner, Ph.D., Associate Professor of Chemistry

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 and Electronic 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-Physical Properties of Ceramic Materials

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

Physical Properties of Ordered and Disordered Solid Solutions

Hartmut Zabel, Ph.D., Assistant Professor of Physics

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

Defects in Solids

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

KC-02-01-01 Structure of Materials

LOCALIZED CORROSION OF PASSIVE METALS

Principal Investigator: Richard C. Alkire
Professor of Chemical Engineering

Supporting Agency: U. S. Department of Energy

Senior Staff: Richard C. Alkire, Professor

Junior Staff: Kirk R. Weisbrod, Research Assistant
Antonia Cangelari, Graduate Student not paid by MRL
Oscar Moreno, Graduate Student not paid by MRL
David Reiser, Graduate Student not paid by MRL
Richard Ulrich, Graduate Student not paid by MRL

ABSTRACT

The purpose of this research is to study disturbances of passive surface layers leading to localized corrosion of metals. The program currently focuses on the sequence by which passivity is regained following disturbance of the surface film. Mathematical models are used to quantify hypotheses based on mass transport, fluid flow, surface reactions and ohmic effects. Experiments aim for controlled variation of system parameters under known corrosion conditions.

Experimental and theoretical results indicate that metal salt films are present during early stages of repassivation. Studies are proposed for broadening understanding of salt film effects in the presence of high-speed fluid flow, and in mixed anion and mixed cation systems. New experimental and theoretical methods are proposed for achieving local depassivation with lasers, and modeling hydrodynamic flow in occluded cell geometries.

PURPOSE

Structural metals are chemically unstable and tend to oxidize spontaneously. For many metals, oxidation causes formation of a protective surface film which, if undamaged, leads to passivity. This project focuses on the nature of disturbances which cause loss of passivity, and on the ensuing process by which passivity is regained, both on the external visible surface and on interior surfaces of pits, crevices and cracks. In particular, we study the dependence of localized corrosion behavior upon transport processes such as mass transfer to aggressive species, ohmic transport of charge, fluid flow, and surface reactions.

Typical disturbances which create loss of passivity include fluid flow, particle impaction, stress cracking, acidification in crevices, and surface inhomogeneities. After birth of local activity, the life and death phases are invariably influenced by transport phenomena. By using

transport models to express hypotheses of corrosion behavior, our program seeks to establish improved levels of quantitative study of corrosion problems. In particular, we are incorporating chemical engineering concepts into models of diffusion- and convection-controlled corrosion processes. By inversion, mathematical models provide a rational basis for predicting conditions under which corrosion may be avoided.

Experimental studies aim for controlled variation of system parameters in order to simplify interpretation of data. Measurements of potential and corrosion rate are carried out in systems for which ohmic resistance and mass transfer coefficients are known. After initiation of disturbance at a passive electrode, the response is followed by electrical and optical measurements which are quantitatively compared with theoretical expectations.

TECHNICAL PROGRESS FY 1980

Most Significant Results

A new experimental technique has been developed for inducing highly localized depassivation in order to study the corrosion of individual pits. The technique employs a low-energy laser beam, focused with glass optics to $\sim 10 \mu\text{m}$ diameter, to trigger depassivation. With this method, it will be possible to study the behavior of single pits and gain more detailed monitoring of events than was previously possible. In addition, the method should enable us to study metals that are not easily depassivated by means previously available (electrochemical depassivation). The method thus provides opportunities for investigation of a much wider range of materials than was previously possible, while simultaneously affording local depassivation on a dimension characteristic of erosion-corrosion by particulates.

Other Results

A very high speed flow system has been developed for studying convective effects on repassivation processes. Capable of achieving Reynolds numbers of $\sim 100,000$, the system permits in situ observation via stereo microscopy and motion picture photography. To date, the system has been calibrated for mass transfer properties with use of $\text{K}_3[\text{Fe}(\text{CN})_6]$ reduction on nickel electrodes. Studies on Fe and Co in H_2SO_4 have illustrated that there is an upper limit on flow rate, above which repassivation will not occur. These results will be compared with theoretical predictions during FY 1981.

An experimental program has been initiated for studying occurrence of salt films in more complex solutions containing mixed cations and mixed anions. Chloride, chlorate, nitrate, sulfate and persulfate systems are under study with Fe and Co electrodes. Studies on cupro-nickels and brasses are in progress since these materials are known to be susceptible to impingement attack.

An extensive literature review of hydrodynamic flow in recesses has been made in preparation for investigation of flow effects on pitting corrosion. Stokes' flow equations can be applied to compute fluid motion in small pits; for simple two-dimensional geometries, Lighthill transformation methods will be used to compute mass transfer rates under the high Schmidt number conditions which prevail. A finite element code is available which incorporates multiple node-point operators and electrode shape change phenomena. These accomplishments constitute the methods needed for major theoretical pursuit.

PUBLICATIONS (Calendar Year 1979):

Theodore R. Beck and Richard C. Alkire
Occurrence of Salt Films During Initiation and Growth of Corrosion Pits
J. Electrochem. Soc. 126, 1662-1666 (1979)
(Also supported by ONR)

MRL SUPPORTED THESES (Calendar Year 1979):

David William Siitari
Experimental and Theoretical Modeling Studies of the Initiation
of Crevice Corrosion
Ph.D. thesis, Chemical Engineering, R. C. Alkire, adviser (1979)

Lee Warren Wiechmann
An Ellipsometric Study of Salt Film Formation during Passivation
M.S. thesis, Chemical Engineering, R. C. Alkire, adviser (1979)

MICROCHEMISTRY OF SOLIDS

Principal Investigators: Charles A. Wert
Professor of Physical Metallurgy
Head, Department of Metallurgy and Mining Engineering

Hamish L. Fraser
Associate Professor of Metallurgy

Supporting Agency: U. S. Department of Energy

Senior Staff: Charles A. Wert, Professor
Hamish L. Fraser, Associate Professor
Barrington C. Muddle, Visiting Assistant Professor
Avigdor Zangvil, Visiting Assistant Professor

Junior Staff: Costas Acrivos, Research Assistant
Kuang-Chien Hsieh, Research Assistant
Arvind Parthasarathi, Research Assistant (Term 12/20/79)
Mark E. Twigg, Research Assistant

ABSTRACT

This research has the aim of characterizing microvolumes of materials using analytical electron microscopy. Three topics are being pursued: (1) determination of crystal structure, crystallographic habit and chemical composition of small precipitates in metallic alloys, (2) examination of metallic and inorganic inclusions in coal and coal conversion products, and (3) development of instrumental techniques which permit such problems to be attacked. We have completed the investigation of the crystal structure and chemical composition of carbides in vanadium of composition near VTi_4C_5 and have determined the range of stability. The coal research involves study of mineral inclusions in coal itself, especially of iron sulfides in coal and coal chars which are residues of liquifaction processing. Technique development involves the following: First, study of instrumental difficulties which limit reliability of the microanalysis--undesired fluorescence in the sample, deleterious effects of surface contamination of the specimens and elimination of x-ray background which reduces sensitivity. Second, understanding of physical processes which permit quantitative interpretation of energy loss peaks. Third, development of on-line computer techniques which permit rapid conversion of experimental data to final results.

PURPOSE

We have continued the development of techniques of microanalysis on a fine scale; in principle, the present state of the art should permit determination of chemical composition and crystal structure of particles in the ten nm range. Also, chemical composition of the light elements, oxygen, nitrogen and carbon, should be possible. Another part is and will continue to

be related to investigations of important alloy systems. In the past, we have concentrated on metallic systems, but a thread of work on geologically important work has been carried on--analysis of compounds in rocks and soils. Part of that work will undoubtedly expand in the future.

The history of development of microanalytical techniques in our laboratory parallel the development, nationally, of microanalytical methods. Initially, we used an electron microprobe, with which we did some interesting studies. The large spot size--about 5 μm --was a severe limitation, since volumes important in science and technology are frequently two orders of magnitude smaller than that. The JEOL-JSEM200 permitted us to make chemical analyses on particles much smaller than that--less than 1 μm , and perhaps 1/10 of that in the best instances. With that instrument we developed a computer-based method of data analysis which permits ratios of elements to be determined accurately and routinely. The program allows for subtraction of background spectra (the so-called "in-hole" spectrum) and subsequent decomposition of the raw spectrum into its constituent parts.

This system suffers from the fact that analysis for light elements is not permitted, since x-rays from these elements cannot be detected using the energy-dispersive x-ray spectrometer fitted on this microscope. To solve this problem, we are continuing to develop methods of light element analysis of all elements except hydrogen and helium. Furthermore, the technique provides an area of analysis as small as 10 nm. We are developing instrumental techniques, applying computer methods of data analysis and carrying out materials programs using this instrument, the VG HB5.

We are continuing our research in three areas: 1) development of experimental methods of making crystallographic and chemical analyses of solid systems using both the JEOL-200 and the VG-HB5. 2) We are continuing examination of metallic alloys, especially carbides and oxides in important metallic systems and adventitious elements such as hydrogen in the transition metals. 3) We are developing methods of analysis of trace minerals in coal, especially the sulfides.

TECHNICAL PROGRESS FY 1980

Most Significant Results

1. Characterization of carbides in binary and multicomponent systems

Characterization of carbides in transition metal systems has been a part of this program for many years. Initially, we were concerned with determining the crystal structure, chemical composition and pertinent crystallographic information about the carbides in the binary systems V-C and Nb-C. We determined that a low temperature sub-carbide is formed below 500°C in these binary systems, and that it is a good strengthening agent at low temperatures. However, it overages readily and is not useful for alloys to be used at high temperatures. A similar result has recently been found by Gareth Thomas and his students in the binary system Ta-C. At higher temperatures, the stable phase Me_2C forms, but it is both incoherent and very coarse, so that it is not an important strengthening agent. High temperature carbides do not form in the binary system, but apparently will readily form in a great many ternary systems. We have examined the carbides in

the ternary vanadium-titanium-carbon alloy and have found it to be highly stable at high temperatures very finely dispersed. Extending this work to studies in other systems might be very fruitful, but we have elected to put more of our research effort into trace impurities in coal. A paper will be published in Metallurgical Transactions which will bring this work to a close.

2. Microanalysis Techniques

Development of microanalytical techniques began with the thesis work of Dr. Zaluzec, who continues to be associated with us in an advisory capacity. Technique development follows two paths: 1) instrument development and 2) computer-aided data acquisition and analysis.

Most of the technique development is taking place on the HB5. The ultra-high vacuum characteristics of that instrument compared with the JEOL 200 make it highly desirable to maintain low surface contamination rates. The HB5 has the characteristic that its vacuum is excellent and the electron gun and lenses ahead of the specimen are highly satisfactory. A very small spot size can be achieved on the specimen. The detection of electrons beyond the specimen is not completely satisfactory. The state-of-the-art spectrometer is not as good as we need, so a new spectrometer is being made which will permit more efficient use of the electrons which pass through the sample and which will reduce the noise at the detector. The detector itself, a photomultiplier tube, has a difficult task.

The range of electron detection which one would like to achieve is at least a million to one, considering the high intensity central beam and the much weaker absorption edges. We are considering addition of new detection systems which will enhance the signal-to-noise ratio in the absorption edges and will still permit measurement of the main beam.

Development of computer-aided data acquisition and analysis is continuing. The goal is to provide a system which can work on the JEOL 200, HB5 and the scanning electron microscopes to permit x-ray and electron counting storage and analysis. Both hardware and software developments are proceeding rapidly.

3. Oxidation-Induced Defects in Ni-Al Alloys

This work has been a continuing part of the program for several years. It is concerned with the effects of oxidation on the physical and mechanical properties of β -NiAl and other intermetallic compounds. The intellectual interest in this subject is interesting, but this Ni-Al compound has technological importance since it is utilized as a coating for jet turbine engine components for oxidation resistance. This work, carried out by Arvind Parthasarathi, has just been completed and a thesis presented. The gist of the work is the following: Excess vacancies are found in the alloy after high-temperature oxidation. These vacancies affect the thermal and mechanical properties of the compound. The origin of these excess vacancies has been in doubt. Some experiments have tended to show that they are introduced during the oxidation process itself. Other experiments tend to show that the excess vacancies are thermal vacancies which are trapped in the material by the rapid quench after the oxidation

process. The present measurements demonstrate that the excess vacancies are, indeed, retained thermal vacancies. However, if the thermal vacancies are maintained at a low level, with little or no supersaturation, the oxidation process does inject vacancies into Ni-Al alloys under certain circumstances. These excess vacancies may form voids and dislocation loops which affect the physical and mechanical properties of the compound. Depending on the thermal treatment of the alloy, the oxide may thus act as a barrier for excess thermal vacancies to diffuse to the surface, but it may itself act as another source of vacancies if the thermal vacancy concentration is small.

4. Microchemistry of Nb-H Alloys

This work has the goal determining the effect of hydrogen on the electronic structure of transition metals using plasmon phenomena. Present work is concerned with observation of the plasmon peak in Nb. This work will be completed in the next year.

5. The Phase Diagram of the Binary System Si,Al/C,N

Nitrides and carbides in the silicon-aluminum system are of considerable technological interest. Basic studies of phases present at high temperature are being carried out in collaboration with the staff of the Materials Laboratory of Wright-Patterson Air Force Base.

6. Mineral Elements in Coal

This study has the goal of determining the chemistry and structure of mineral compounds in coal. The work is concerned with ultra fine particles which can be observed and studied in the scanning electron microscope and the transmission electron microscope. Ample studies of gross mineral composition are being carried on in many laboratories in the world. Our work is aimed at studying the very fine particles of compounds such as sulfides, oxides and carbonates which may be technologically important in coal conversion processes. Two goals have been achieved this year. We have examined many specimens of coal in the scanning electron microscope to familiarize ourselves with the overall nature of inclusions in the micron and sub-micron range. Many other laboratories have done this and are continuing to do so. The chief thrust of the work, though, is microanalysis of trace elements in the transmission electron microscope, an area of competence which most conventional coal laboratories do not possess. We have learned to thin coal specimens for the electron microscope and have made a number of investigations of crystal structures and composition of some of the common compounds, principally the sulfides. Specimen preparation is very difficult, since coal cannot be thinned using electrolytic methods, we are used to employing in metallic systems. However, we have successfully prepared specimens using ion milling and can determine trace element compositions and crystal structures. The chief difficulty with specimen preparation is the extraordinary brittleness of coal, and many specimens break during preparation and handling. However, we do have about one dozen specimens containing various compounds in states of dispersion. Fortunately, ion milling seems to thin the coal and the trace element compounds about uniformly, so that one can see through the compounds about in the same way as one can for the coal matrix, itself.

RELATIONSHIP TO OTHER PROJECTS

This research relates to several other research projects.

H. Fraser:

1. With Robert Mehrabian ARPA DAAG-46-76-C-0023.
Microstructure of Rapidly Solidified Metals.
2. Pratt and Whitney Aircraft (Sub-contract of an Air Force Project).
Microcharacterization of Rapidly Solidified Metal Powders (Nickel-based Superalloys).

C. Wert

1. NSF DMR-73-02581. Elastic Properties of Niobium Containing Hydrogen.
2. The research on coal is being carried out in collaboration with coal-scientists of the Illinois State Geological Survey (Coal Resource section headed by Dr. Heinz Damburger. We are working specifically with Suzanne Russell, a geologist and chemist).
3. NSF DMR-78-07761. Microcharacterization of Oxides and Nitrides in Niobium.

PUBLICATIONS (Calendar Year 1979):

S. Bruemmer, C. P. Fluhr, D. Beggs, H. L. Fraser, and C. A. Wert
An Electron Microscopy Study of the High Temperature Carbide Formed
in a V-5Ti-C Alloy
Metall. Trans. A (in press)

H. L. Fraser and J. B. Woodhouse
Energy-Dispersive X-ray Analysis Using a Field Emission Gun: A Precaution
Proceedings of a Specialist Analytical Microscopy Workshop, 191 (1979)

N. J. Zaluzec and H. L. Fraser
On the Effect of Contamination in X-ray Microanalysis
Proceedings of the Analytical Electron Microscopy Workshop, 122 (1979)

MRL SUPPORTED THESES (Calendar Year 1979):

Nestor John Zaluzec
An Analytical Electron Microscope Study of the Omega Phase Transformation
in a Zirconium-Niobium Alloy
Ph.D. thesis, Metallurgical Engineering, H. L. Fraser, adviser (1979)

THEORY OF POLYMERS

Principal Investigator: Richard J. Gaylord
Assistant Professor of Metallurgical Engineering

Supporting Agency: U. S. Department of Energy

Senior Staff: Richard J. Gaylord, Assistant Professor

ABSTRACT

We are studying a number of theoretical problems in the statistical mechanics of polymers. One topic is the behavior of confined polymer chains. We have modeled the amorphous component of semicrystalline polymers, filled or reinforced elastomers and block copolymers by considering a "two wall" model of polymer chains confined between parallel walls. The theoretical treatment incorporates the configurational statistics of the various chains which may occur (loops, cilia, floating chains and bridges), the short-range hard sphere repulsive and the long-range attractive interactions between chain segments and the van der Waals forces between wall surfaces. The model explains, in a consistent manner, a wide range of deformation features which are characteristic of bulk polymers, including the Young's modulus, yield, stress softening, draw, stress hardening, the Mullins effect, set and craze or crack propagation.

PURPOSE

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 crosslinked 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 confining material.

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

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(1) Having established the usefulness of our two wall model, we propose to refine it. Specifically, a more detailed description of the confined chain segment interactions and its incorporation into the statistics of the confined chains in a self-consistent manner will be sought. The achievement of this goal will enable the theory to make detailed predictions of the mechanical deformation properties of heterogeneous polymeric systems as a function of external variables, such as temperature and strain, and as a function of internal variables, such as the morphology of the amorphous material within the polymer. This will provide the polymer technologist with a recipe for developing polymeric materials with specific deformation properties.

(2) We are attempting to establish the general formalism for the birefringence of a polymeric chain confined by any number of rectilinear, impenetrable walls. This will then be used to calculate the birefringence of bridges, loops, cilia and floating chains which are confined between two infinite parallel walls. When the birefringence properties of the two wall model are known, it will be possible to predict the optical properties of heterogeneous polymeric systems as a function of temperature, strain and amorphous structure. This will be valuable for the further development of polymeric materials.

RELATIONSHIP TO OTHER PROJECTS

Our theoretical work is related to the experimental work of several faculty in the Materials Research Laboratory at the University of Illinois.

T. J. Rowland is examining semicrystalline polymers and elastomers.

J. Jonas is studying polymer chain entanglements.

PUBLICATIONS (Calendar Year 1979):

R. J. Gaylord

Entanglement and Excluded Volume Effects in Rubber Elasticity
Polymer Engineering and Science (in press).

R. J. Gaylord

The Confined Chain Approach to the Deformation Properties of Bulk Polymers
Polymer Engineering and Science (in press).

R. J. Gaylord

A Simple Model for the Stress-Strain Behavior of the Interdomain Component
of Block Copolymers

J. Macromolecular Science-Physics (submitted to).

SEMICONDUCTOR CRYSTAL GROWTH BY ION BEAM SPUTTERING

Principal Investigator: Joseph E. Greene
Professor of Metallurgical Engineering

Supporting Agency: U. S. Department of Energy

Senior Staff: Joseph E. Greene, Professor
Atef H. Eltoukhy, Research Engineer (until 2/2/80)

Junior Staff: Lydia Rivaud, Research Assistant

ABSTRACT

This is a new project in which we propose to investigate the growth kinetics, physical properties, and structural stability of unique metastable semiconducting thin films. We have recently demonstrated the growth of single crystal $\text{InSb}_{1-x}\text{Bi}_x$ and $(\text{GaSb})_{1-x}\text{Ge}_x$ films, which represent two subclasses of these metastable alloys. The underlying feature which allows the growth of such materials is the use of controlled low energy (25 to 250 eV) ion bombardment of the substrate and growing film during vapor phase deposition. Thus the study of energetic particle-surface interactions is a central theme of our research. Ion bombardment during film growth results in significant modifications of elemental sticking probabilities, adatom surface mobilities, film nucleation characteristics, island coalescence, and ultimate film structure. The resulting single crystal metastable films can be thermally stable to several hundred °C and they exhibit unique electro-optic properties.

We believe that this work will lead to the development of an entire new class of semiconducting materials, thereby increasing the range of available materials properties to answer the needs of ever more stringent materials requirements in the future decade.

PURPOSE

Materials requirements for active layers in thin film electro-optic devices such as photodetectors and solar cells are becoming ever more stringent and design parameters for optimum efficiency are often difficult to achieve with conventional materials technology. Metastable materials exhibiting a high degree of thermal and temporal stability offer the possibility of extending the range of achievable properties. Amorphous Si, belonging to one subclass of metastable semiconductors, has already generated considerable scientific interest as a candidate for inexpensive solar cell applications. In addition to structural metastability, alloy semiconductors have been grown which are chemically metastable by virtue of exceeding the equilibrium solid solubility limit. For example, we have recently grown single crystal $\text{InSb}_{1-x}\text{Bi}_x$ alloys with InBi concentrations up to 12 mole %, approximately five times the solid solubility limit. This is actually a case of combining both structural and chemical metastability since InBi has a tetragonal crystal structure but is forced to crystallize in the usual III-V zinc blend sphalerite structure in the metastable alloy. The addition of InBi decreases the direct InSb band gap linearly from 0.19 eV at 20°K to become a semi-metal at about 12 mole % InBi. The metastable alloy has already shown promise as a bolometer and far-IR detector.

This research program is directed towards developing an understanding of the detailed mechanisms associated with the growth of single crystal metastable semiconducting alloys. The kinetics of crystal growth, the thermodynamics of metastable-to-metastable and metastable-to-equilibrium phase transformations, and physical properties of deposited films will be investigated and the results correlated in order to develop a generalized model of metastable film growth. The model will not only be useful in developing a better understanding of metastable materials, but also for predicting growth conditions and expected stability limits for the deposition of metastable films with a desired set of properties. In order to couple effectively with the extensive background our group has developed in the area of crystal growth of III-V alloys by sputtering, we will initially investigate III-V based metastables such as $\text{InSb}_{1-x}\text{Bi}_x$, $(\text{GaSb})_{1-x}\text{Ge}_x$, and $\text{In}(\text{N},\text{O})$. However, we intend to apply the results of this work to investigate the growth of metastable II-IV-V₂ chalcopyrate systems which offer promise for photodetector and solar cell applications.

Film growth experiments will be carried out both in ultra-high vacuum multi-target ion beam sputtering (IBS) and molecular beam epitaxy (MBE) systems in which the growing film can be subjected to controlled low energy ion bombardment using a neutralized beam, and to local laser heating during deposition. In situ investigations will be made of nucleation, island structure and coalescence, and elemental sticking probabilities. The chemistry and physical properties of as-deposited films will also be correlated with film growth parameters. The thermal and temporal stability of the films will be explored using post deposition furnace and laser annealing techniques and calorimetric measurements will determine metastable phase diagrams.

The limitations on the growth of metastable materials are both energetic and kinetic in nature. Namely, the excess enthalpy in a metastable solid material must not exceed the enthalpy of melting, and the atomic mobility must be sufficiently low to prevent the nucleation and growth of a more stable phase. The upper limit on the allowable excess energy of a metastable phase is not a severe restriction since the enthalpy of melting is generally much larger than the energy difference between various metastable and stable phases. For example, the energy difference between amorphous Ge and its equilibrium crystalline phase is approximately 50 meV per atom. It is this small energy difference between phases which allows the possibility of growing such materials. On the other hand, the fact that the energy differences between competing structures is so small leads to difficulty in computational methods, using such techniques as pseudopotential calculations, for establishing theoretical stability conditions.

The kinetics of metastable phase formation during thin film growth are determined by the relative elemental rates of deposition, adatom surface diffusion, and incorporation into the lattice. Given a total deposition rate of $R(\text{\AA}/\text{sec})$, a typical adatom may diffuse on the surface for a time $t \sim a/R$, where a is the average jump distance, before it becomes surrounded and restricted by co-deposited atoms. Thus the mean diffusion distance may be estimated as

$$\bar{X} = (2D_s t)^{1/2} = a(2\nu \frac{a}{R})^{1/2} \exp(-Q_s/2kT),$$

where D_s is the surface diffusivity, ν is the jump frequency, and Q_s is the activation energy for surface diffusion. There have been very few measurements

of Q_s , but available data for metal atoms indicate that it is on the order of 0.5 eV. Taking $v = 10^{13}$ /sec, $a = 3\text{\AA}$, and $R = 5\text{\AA}/\text{sec}$, one finds $\bar{X} \sim 930\text{\AA}$ at 300 K. However, even a small change in the value of Q_s to 0.8 eV alters $\bar{X}$ by almost three orders of magnitude to a value of only $2\text{\AA}$. This indicates why the choice of substrate crystal structure and orientation, as well as changes in the kinetic energy of condensing species and the flux and energy of ion bombardment at the growth interface, may critically alter the growth kinetics and lead to the establishment of metastable phases. It also indicates that careful measurements of atomic surface mobility and its temperature dependence as a function of deposition parameters are essential for understanding metastable growth kinetics.

A central focus of this work will thus be to develop a detailed understanding of energetic particle-surface reactions. It is the use of low energy (25-250 eV) ion bombardment of the substrate and growing film which stabilizes the growth of single crystal metastable alloys. Such bombardment greatly affects film nucleation kinetics through the development of preferred adsorption sites and enhanced adatom mobilities. We have developed techniques for measuring diffusion over very short distances, $< 100\text{\AA}$, and have observed enhancements in diffusion coefficients of several orders of magnitude due to low energy ion bombardment. We have also shown that elemental incorporation probabilities--which can now be expressed as $\sigma_i = \phi_i(1 - \Gamma_i)$ where σ is the incorporation probability of element i into the growing film, ϕ_i is the thermal sticking probability, and Γ_i is the resputtering probability--can be drastically altered from equilibrium thermodynamic values by preferential resputtering. Crystal structure and preferred orientation are also affected by low energy ion bombardment.

RELATIONSHIP TO OTHER PROJECTS

This work would not be possible without extensive use of the excellent analytical facilities available in MRL. In addition, we interface closely with several other research groups both on and off campus. Photoluminescence measurements on our samples are carried out in collaboration with Professor B. Streetman of MRL. We have also established a joint effort with Dr. P. Williams of the MRL on ion bombardment enhanced interfacial diffusion. Studies using XPS to obtain chemical bonding information are carried out at UOP, Inc. in Chicago in collaboration with Dr. Terry Barr. Finally, we have an ongoing interaction with Dr. Carlos Mammana at the University of Campinas in Brazil and Dr. G. Bajor at the Technical University of Budapest in Hungary.

PUBLICATIONS (Calendar Year 1979):

K. C. Cadien, J. L. Zilko, A. H. Eltoukhy, and J. E. Greene
Growth of Single Crystal Metastable in $\text{Sb}_{1-x}\text{Bi}_x$ and $(\text{GaSb})_{1-x}\text{Ge}_x$ Films
J. Vac. Sci. Tech. (in press)

DYNAMIC STRUCTURE OF MATERIALS UNDER EXTREME CONDITIONS OF TEMPERATURE
PRESSURE

Principal Investigator: Jiri Jonas
Professor of Chemistry

Supporting Agency: U. S. Department of Energy

Senior Staff: Jiri Jonas, Professor
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ABSTRACT

NMR relaxation techniques and laser Raman scattering experiments are used to study the effects of high pressure and high temperature on the dynamic structure of the following main classes of materials: 1) amorphous polymers; 2) fluids and molten salts; 3) supercooled metals; 4) lithium intercalation compounds of layered titanium disulfide. Current NMR studies dealing with the structure - property relationship in polymeric systems focus on the problem of the effects of crosslinking and molecular entanglements on the dynamic behavior of polymers. Experiments on well-characterized polymer samples are designed to improve our molecular level understanding of elastomers and to test various molecular and phenomenological theories of the elastic behavior of polymeric networks. Systematic laser Raman scattering experiments on molecular fluids concentrate on the problem of vibrational dephasing in polyatomic molecular liquids and on the ordering phenomena in polar liquids. Continued development of unique measurement techniques for experiments at extreme conditions of high pressure and high temperature represents an important aspect of our research effort. Our studies of the dynamic structure of compressed supercritical fluids are continuing with experiments proposed to investigate compressed supercritical water and aqueous solutions. Various NMR experiments are planned to investigate transport properties of undercooled liquid metals to gain a better understanding of the different solid structures that can be produced during solidification at high undercooling. The objective of the exploratory high pressure NMR experiments on lithium intercalation compounds of layered titanium disulfide is to characterize better the Li-TiS₂ interaction in these materials.

PURPOSE

Study of the dynamic structure of various disordered materials at high pressure and high temperature represents the main theme of our research. The following classes of materials are currently investigated: 1) amorphous polymers; 2) fluids and molten salts; 3) undercooled metals; 4) lithium intercalation compounds of layered titanium disulfide.

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. One may point out that all our various directions of proposed research are identified as having high priority in the above document. In the following sections, references to this document are made.

The main technique we currently use is the nuclear magnetic resonance (NMR) spectroscopy which represents a powerful tool for investigation of motion 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 have 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. or abroad with comparable performance features of the NMR experimental system. Further development of new instrumentation for work at the extreme conditions of high pressure and high temperature represents an important aspect of our work.

In our NMR studies of polymers, we are currently interested in following the effects of permanent crosslinks and molecular entanglements of various motions in polymers. An important outcome of our studies is the observed sensitivity of some of the relaxation parameters to network formation. 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. Our experiments on well characterized polymer samples enable us to test various molecular and phenomenological theories of elastic behavior of polymeric networks. 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 to polymers (see, e.g., p. 18, Materials Science Overview I).

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. 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 Science 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). There is an 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 Science Overview, I).

The important problem of transport in undercooled liquid metals (p. 5, Materials Science Overview, I) can only be attacked because of the experience we have gained in different areas of NMR instrumentation applied to the study of the dynamic structure of liquids, and because of the recent development (Perepezko, Rasmussen, 1977) in preparation of stable droplets of low melting metals and alloys in a carrier fluid. These emulsification procedures suppress heterogeneous nucleation of the liquid metal and permit maximum undercooling which is then limited by a homogeneous nucleation. To measure diffusion in these undercooled metals (Sn, Pb, Bi, etc.), we shall use the NMR rotating frame relaxation techniques which we have successfully employed to study very slow motional processes in liquids, polymers, and solids. Expertise in high temperature NMR techniques represents another necessary prerequisite for the planned experiments. In addition, our results dealing with the applicability of various hydrodynamic equations at the molecular levels in liquids, including highly viscous liquids, will be used to predict viscosity of undercooled liquid metals. The progress we make in studying diffusion in undercooled liquid metals and alloys will contribute toward a better understanding of different solid structures that can be produced during solidification at high undercooling.

The long range objective of our laser Raman scattering studies of liquids is to improve our understanding of the liquid state and the liquid-solid state transitions in particular. Our recent experimental evidence indicates the possibility of some degree of ordering in polar liquids before the freezing point is reached.

The feasibility of high pressure NMR experiments on lithium intercalation compounds of layered titanium disulfide has very recently been demonstrated in our laboratory. Experiments are planned to investigate the detailed nature of Li-TiS₂ interactions. These studies are of relevance to technological efforts towards the development of high energy batteries (p. 5, Materials Science Overview, I).

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Most Significant Results

1) Nuclear magnetic resonance spectroscopy represents a unique, well-established tool for investigation of motions at the atomic and molecular level. Main motivation for our experiments on polymers is to correlate the molecular level dynamic information obtained by NMR with the bulk properties of polymeric networks. Our current research follows three main directions: i) crosslinking effects at the molecular level, i.e., permanent network formation; ii) entanglement effects at the molecular level, i.e., transient network formation; and iii) correlation between the bulk macroscopic properties of polymers and the molecular level dynamic information as observed by NMR. We have obtained results on the first two of these main problems and the third is now under investigation.

In the last report to DOE, we discussed the results of our NMR study of cis-1,4-polybutadiene samples with different crosslink density (G. C. Munie, J. Jonas, T. J. Rowland). We found that the spin-spin relaxation times, T_2 , and the free induction decay per se are very sensitive to network formation and are well suited for characterization of chemically crosslinked samples.

As a continuation of our research program, we have investigated the effects of molecular entanglements, i.e., transient network formation, on the dynamic behavior of well characterized samples of polybutadiene.

Proton relaxation measurements have been used to investigate the effect of entanglements on segmental motion in polybutadiene samples of narrow molecular weight distribution. The temperature and pressure dependencies of the proton spin-lattice relaxation time, T_1 , the proton spin-spin relaxation time, T_2 , the the spin-lattice relaxation time in the rotating coordinate frame, $T_{1\rho}$, were reported. Use of these various relaxation times allows us to probe frequencies of molecular motions from very low frequencies to the MHz region. The three polybutadiene samples have weight average molecular weights of 2,700, 17,000 and 423,000. These values are below to well above the reported values of molecular weight for entanglements. The relaxation data are interpreted to terms of the effects of entanglements on segmental chain motion. Because of their sensitivity to low frequency motions, the T_2 data are of special interest. At temperatures above the T_1 minimum, the small T_2 temperature dependence reported earlier for crosslink samples is found only in the highest molecular weight sample. This solid-like behavior of T_2 reflects the non-zero averaging of dipolar interactions due to anisotropic motion of the chain segments between entanglements. To illustrate the sensitivity of the observed proton T_2 values to the entanglement effects, we present Figure 1 which gives the normalized T_2 values vs. number average molecular weight.

Fig. 1. Effect of molecular entanglements on overall chain mobility in cis-1,4-polybutadiene. The observed T_2 for different polybutadiene samples is normalized with respect to the T_2 observed for low molecular weight entanglement free sample. $\bar{M}_N$ represents the number average molecular weight.

In addition, by the use of pressure as a variable, the transient nature of the entanglement can be clearly demonstrated. Pressure and temperature variables also make it possible to separate the volume and thermal effects on the molecular motions. By using pressure as a variable, the activation volume $\Delta V^\ddagger$ for the various relaxation processes have been calculated. We find that $\Delta V^\ddagger$ for T_1 increases with temperature whereas the $\Delta V^\ddagger$ for T_2 and for T_{10} are found to decrease with temperature in agreement with reported $\Delta V^\ddagger$ values obtained for viscoelastic and dielectric measurements. The reason why the temperature behavior of $\Delta V^\ddagger$ for T_1 is different from that obtained for T_2 , T_{10} , viscoelastic and dielectric relaxation measurements, is related to the fact that T_1 is determined by high frequency localized chain motions whereas the other relaxation parameters reflect low frequency motions.

2) Relaxation processes in molecular liquids represent an area of high current interest. Our systematic laser Raman scattering experiments on polyatomic molecular liquids focus on the nature of vibrational broadening of the isotropic line shape. These experiments are designed to provide the experimental data necessary for testing the various theoretical models.

The broadening of isotropic Raman band shapes may be influenced by several mechanisms. The two dominant ones involve energy relaxation via inelastic collisions and phase relaxation via quasielastic collisional processes. In the inelastic collisional process, the energy levels of the molecule change, whereas the quasielastic collision causes only a phase shift in the wave function while the molecule remains in the same energy level. Fischer and Lauberau and Oxtoby and Rice used a collinear isolated binary collision model and considered only the repulsive part of the intermolecular potential to calculate dephasing and only the repulsive part of the intermolecular potential to calculate dephasing and population relaxation times.

There have been quite a number of different theoretical models proposed to relate the line width of the isotropic line shape to other quantities characteristic of the liquid. We have tested the different theoretical models and found the dephasing model, based on the isolated binary collision model as proposed, e.g., by Fischer and Lauberau (1976) describes the experimental data very well. In spite of the fact that we used a model originally developed for diatomic molecules to interpret data on polyatomic molecular systems, we may conclude that this model reproduces the essential features of the density and temperature behavior of the observed vibrational dephasing rates as obtained in our spontaneous Raman experiment provided that one uses the Enskog relaxation time as the time between collisions. One has to emphasize that the Enskog relaxation time gives a good estimate of the time between collisions in liquids, and thus no corrections for many body effects are needed. We found good agreement for Si-C, C-H in $\text{Si}(\text{CH}_3)_4$, CH_3CN , CHF_3 ; analogous agreement was obtained for CD_3CN , CDCl_3 , CHCl_3 , and also CH_3OH .

Our recent Raman study of liquid isobutylene provided results which will have significant impact on the basic theory of vibrational dephasing and influence further work in this area. The Raman line shapes of the ν_4 (A_1) symmetric $\text{C}=\text{CH}_2$ stretching mode at 1657 cm^{-1} and the ν_9 (A_1) symmetric $\text{C}-\text{CH}_3$ stretching mode at 805 cm^{-1} in isobutylene have been measured as a function of pressure from vapor pressure densities to 0.8 gcm^{-3} over the

temperature range from -25°C to 75°C . The frequency shifts of the above isotropic bands have also been determined under the same experimental conditions.

The important experimental finding is the opposite effect of density on the isotopic line widths of the C-CH_3 and C=CH_2 stretching vibrations; namely, the former band broadens with increasing density whereas the latter band narrows with increasing density under isothermal conditions. Such narrowing is unexpected in view of the theoretical and experimental results on the mechanism of vibrational broadening. A very different behavior is also observed for the frequency shifts of these two stretching modes. There is a large red gas-to-liquid shift for the C=CH_2 band while its frequency changes very little with density over the liquid range studied. The opposite is true for the C-CH_3 band which has a small gas-to-liquid shift but exhibits a large blue shift with increasing density in the liquid region. A qualitative interpretation of the experimental frequency data is based on consideration of classical vibrational amplitudes of the two vibrations and the infrared activity of the C=CH_2 mode.

The experimental vibrational widths are discussed in terms of available theoretical models for dephasing and other mechanisms for broadening of isotropic Raman line shapes. It appears that the behavior of the C-CH_3 band can be best interpreted in terms of the isolated binary collision model for dephasing whereas the unusual density effects on the line widths of the C=CH_2 band are discussed in a more general way using the Kubo stochastic line shape.

It appears that no single theoretical model can explain satisfactorily the line shape behavior of all vibrational models even in simple polyatomic molecular liquids.

3) Fini and Mirone (1976) have shown that the frequencies of the polarized (VV) and depolarized (VH and HV) spectra do not coincide for certain vibrations in a number of molecules. They show in their paper that the necessary condition for this phenomenon are: i) large permanent dipole moments of the molecules ($\mu > 2D$); ii) large infrared activity of the vibrations. It was concluded that the ν (VH-VV) shift is associated with the existence of coupled oscillators. According to their model, the molecules are ordered to some extent due to their strong dipole moment thereby enabling the coupling of vibrations of neighboring molecules, via the transition dipole (TD) moment. If we consider two molecules coupled by the TD mechanism, we realize that the vibrational frequency will split into two, corresponding to the in-phase and out-of-phase vibrations of the system. For a solid lattice, the magnitude of this frequency splitting (Davidov splitting 1971) was calculated by Hexter (1960). No explicit calculation for a liquid has been performed up to now.

The investigation of the frequency splitting may be potentially a powerful tool for studies of short range molecular order in liquids, especially, if the results are considered together with measurements of vibrational frequency shifts and of isotropic line shapes. Therefore, we carried out a detailed investigation of the polarized and depolarized spectra of the CO stretching vibration in liquid acetone and liquid acetaldehyde over a wide

range of densities and temperatures. Dilution experiments in cyclohexane have also been performed. The experimental data were interpreted in terms of a model for dipole coupling proposed by Khuen and Doge (private communication), and we conclude that the different frequencies of the VH and VV Raman bands originate from the dipole coupling within molecules. We have shown that factorizing of the radial and the angular distribution functions introduces no serious error in the theoretical model for dipolar coupling. It was also confirmed in a direct way that anharmonic terms are more important in band shifts and broadening than the pure TD-TD terms. Experiments on additional molecules with dipole coupled vibrations are underway in order to better understand this interesting phenomenon in polar liquids.

Other Results

1) As a continuation of our studies of the dynamic structure of liquids, we have investigated the proton spin-lattice relaxation times, T_1 , in water over a wide range of temperatures and densities. The higher pressure experiments at temperatures above 300°C were performed using a special high-pressure, high-temperature NMR probe (T. H. DeFries and J. Jonas, 1979). The intramolecular and intermolecular dipolar relaxation and the spin-rotation interactions represent the main relaxation mechanism contributing to the observed proton T_1 . Figure 2 illustrates well the general experimental trends in the

Fig. 2. Proton spin-lattice relaxation time, T_1 , in H_2O plotted as a function of density over the temperature range from -15°C to 700°C.

T_1 data reflecting the opposite density dependence of the spin rotation and dipolar contributions. At lower temperatures where the dipolar mechanism dominates, the slope of the T_1 vs. density, ρ , is negative, whereas at higher temperatures, the spin rotation mechanism dominates and the T_1 vs. ρ is positive. From Fig. 2, one can also follow the intermediate temperature region where both the spin rotation and dipolar interactions contribute. Work is in progress to interpret theoretically this unique experimental data on water and improve our understanding of this important but complex and anomalous fluid.

2) The NMR work on polymers as discussed above, provides a basis for the work now in progress on bulk elastomer properties. Polybutadiene networks of varying crosslinked densities have been prepared using dicumylperoxide. These networks are divided along two different lines. First, crosslinking has been done under two states of dilution. Networks have been prepared using both bulk crosslinking (no diluent) and crosslinking in the diluted state. This allows one to obtain networks in an entangled (bulk) state and relatively entanglement free (dilute) state. Secondly, networks have been prepared from two different molecular weights of polybutadiene: a low molecular weight relatively entanglement free polymer and a high molecular weight heavily entangled polymer. Bulk property measurements of swelling behavior, stress-strain behavior, density, and sol fraction content allow calculation of both the C_1 and C_2 terms in the phenomenological Mooney-Rivlin (1948) expression for elastic behavior and the determination of crosslink density. These measurements are now in progress. It should be mentioned that the stress-strain behavior is being examined for network in which the sol fraction is present and absent (via extraction techniques). This is being done to test current theories of network behavior (R. J. Gaylord 1979).

Upon completion of the mechanical, bulk property measurements, NMR will be used to examine the effects of molecular weight, sol fraction, and dilution on motion at the molecular level. Since crosslinking has been done over a range and has been measured, the presence or absence of entanglements should be observable via NMR. These entanglement effects will then be examined relative to measured C_2 values and thus enable us to test the current theories of elastic behavior and particularly the ideas concerning the entanglement basis for the C_2 term.

3) A major instrumentation effort has concentrated on design and building of new high pressure, variable temperature NMR probes and the entire new NMR spectrometer system to be used with the acquired superconducting magnet system [funded by NSF(75%) and by the University of Illinois (25%)]. At the present time, the spectrometer is operable, and we have solved the main problems in design of high pressure NMR probes suitable for work in superconducting magnets. Exploratory experiments were carried out on undercooled metals, the signal has been observed for ^{209}Bi after the receiver recovery time was improved (currently 5 μsec). In addition, a special NMR probe suitable for high pressure work on Li_xTiS_2 was designed, built, and tested, and preliminary feasibility experiments on intercalation compounds were carried out.

An additional instrumentation development is underway to allow us to use high resolution NMR spectroscopy (line widths smaller than 2 Hz at 180 MHz) at extreme conditions of high pressure and high temperature. This development will open a new area of NMR experiments at high pressure.

RELATIONSHIP TO OTHER PROJECTS

Concerning the relationship of our research to other projects, one has to consider two main facts. First, because our high pressure and high temperature NMR experiments are unique, there is no duplication of our effort with laboratories elsewhere in the U.S.A. and abroad. Second, the unique performance features of our experimental setup are the very reasons which may lead to growing collaboration with researchers at this campus and elsewhere in the U.S.A.

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 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.

An NMR study of the effects of crosslinking on molecular motions in various samples of cis-polybutadiene with well defined crosslink density has been carried out in a collaborative effort with Professor T. J. Rowland (Department of Metallurgy and Mining, University of Illinois). In our current project dealing with the nature of molecular entanglements and permanent crosslinks in various polymer systems, we are greatly helped by Professor R. J. Gaylord (Department of Metallurgy and Mining, University of Illinois). The current and proposed studies of polymers do not represent an isolated effort because a strong group of researchers works in the area of polymer materials at the University of Illinois.

Some phases of the planned studies of diffusion in undercooled liquid metals will be carried out as a collaborative effort with Professor J. H. Perepezko (Department of Metallurgical and Mining Engineering, University of Wisconsin-Madison). This specific project may grow significantly in scope and extent with an increasing degree of collaboration with researchers in metallurgy.

Our exploratory experiments on intercalation represent a collaborative effort with Dr. B. G. Silbernagel (Exxon Research and Engineering Company).

Beyond actual collaboration on joint projects, frequent research discussions with various members of the Materials Research Laboratory at the University of Illinois greatly help our research effort. In particular, daily discussions with Professor H. G. Drickamer (Department of Chemical Engineering, University of Illinois) prove extremely valuable.

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NMR Relaxation Study of Crosslinked cis-1,4-Polybutadiene
J. Polymer Science (accepted for publication)

W. Schindler and J. Jonas
Density and Temperature Effects on Vibrational Phase Relaxation and
Frequency Shifts in Liquid Isobutylene
J. Chem. Phys. (accepted for publication)

W. Schindler, P. T. Sharko, and J. Jonas
Raman Study of Dipolar Coupling Effects in Polar Liquids
J. Chem. Phys. (submitted to)

KC-02-01-02 Mechanical Properties

HYDROGEN BEHAVIOR IN BCC METALS

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ABSTRACT

The mobility of hydrogen and its isotopes and their effects on the properties of bcc metals are being studied using several methods. Emphasis is being placed on understanding the quantum diffusion behavior of these light interstitials and on determining the H-H and H-lattice interactions. The unit processes in this diffusion behavior, namely the motion of hydrogen in a delocalized (100) ring and the hopping between rings has been characterized for hydrogen trapped at O and N interstitials using anelastic measurements and neutron scattering. The relationships between the behavior of trapped H and long range diffusion of H is being studied using Gorsky effect techniques. The behavior of untrapped hydrogen is much less well understood because of the difficulty in studying its low temperature behavior. Nonetheless it is of major importance in diffusive processes and we are continuing to study its behavior. Two new techniques, anelastic piezoresistance and the analogous electron scattering induced transitions are being applied to these investigations.

The mobility of hydrogen at the metal-gas surface is being explored using the combined techniques of Raman spectroscopy, Auger analysis and permeation methods. We are determining the vibrational modes of H, its interactions with absorbed surface species such as SO₂, H₂S and H₂O, and the effect of these factors on the rate of entry of hydrogen into the solids. In addition, the effects of surface structures such as dislocations, grain boundaries and surface orientation induced facets on hydrogen entry are to be determined.

The properties of hydrides and phase transitions in hydrides are being investigated using TEM, electron and neutron diffraction. The emphasis is on hydrogen density waves and the nature of the phase transitions which result from their interactions with the lattice.

PURPOSE

Our program focusses on the mobility of light interstitial elements in solids and on the effects of these interstitials on the properties of solids. We have chosen to study the Group V B elements Nb, Ta and V and their alloys with hydrogen and its isotopes because (a) their behavior is characteristic of many bcc-H systems, (b) we have good metallurgical control over the purity and perfections of the required crystals, (c) large hydride crystals of controlled compositions can be grown, and (d) a large and expanding body of information concerning these systems is available. In our research we have examined the mobility of hydrogen and its isotopes over a wide range of temperatures using a variety of experimental techniques which are discussed below. In addition to examining the hydrogen diffusion mechanisms we are attempting to understand the nature of the interactions between hydrogen interstitials and between hydrogen and the metal lattice. We would like to establish (a) the nature of solute hydrogen in the bcc lattice (i.e., is it a localized or delocalized interstitial), (b) the mechanisms by which it moves through the lattice and across the gas-solid interface, and (c) the behavior of hydrogen in ordered systems (hydrides) particularly during phase transitions.

This area of research provides a fortunate confluence of basic and applied research problems. The behavior of light interstitials is governed by quantum effects and hence is of significant theoretical interest. A number of theories purporting to describe the diffusion of light interstitial solutes have been and are being developed and the systems which we are studying provide critical tests for these concepts. At the same time, the mobility of hydrogen, its effects on the properties of solids, 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. The systems we study are not always directly used in engineering applications, but the phenomena we are discovering are of direct interest and will provide a necessary basis for engineering design.

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 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.

Energy storage technology is another area with which our research is closely interactive. 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.

In our program we are studying the mechanisms of hydrogen mobility in solids over a wide range of temperature. The higher temperature ranges are of direct interest in that they correspond to the range of active hydrogen embrittlement and stress corrosion. The lower temperature ranges are of interest in understanding quantum effects in diffusion and in developing our phonon assisted tunneling model. The entrance of hydrogen into the metal from the gas phase or from an aqueous corrosive environment is controlled by surface reactions. We are studying these with a particular emphasis on hydrogen entry from the gas phase and the effects of adsorbed molecular species such as H_2S , SO_2 , O_2 and H_2O . In addition we will be examining the effects of structural features such as grain boundaries and dislocations on these processes. Many of these processes are known to be of importance in technological processes. For example, traces of H_2S are known to accelerate hydrogen embrittlement of steels while H_2O and O_2 stop crack propagation. The effect of hydrogen on the atomic bonding is a central question in the area of environmental effects on fracture. Our work addresses this question by examining the phonon structure of the metal hydrogen systems and particularly of the hydrides. Interactions between hydrogen atoms and between hydrogen and the lattice determine the ordering processes and phase transitions in the hydrides which are being studied. In addition, the properties of the hydrides are of intrinsic interest as they form and cleave under stress during hydrogen embrittlement and during the hydriding and de-hydriding processes in energy storage systems.

Mobility of the light interstitials in bcc metals is dominated by quantum tunneling effects. Theory indicates that at temperatures above about $\theta_D/2$ (θ_D is the Debye temperature) the temperature dependence of the diffusivity is approximated by a classical Arrhenius temperature dependence, while a decreasing dependence on temperature is expected at $T < \theta_D/2$. This behavior has been shown to occur experimentally for the motion of trapped H in the Nb-U-H and Nb-N-H systems. Over the entire temperature range the isotope effect is very much larger than the classical square root of the mass ratio dependence again indicating a nonclassical motion of the hydrogen. In order to account for this quantum tunneling behavior, we have developed a model of hydrogen behavior in bcc metals which is based on a delocalized hydrogen interstitial. The hydrogen occupies a set of tetrahedral and triangular sites forming a "ring" on the (100) face of the unit cell and tunnels between these sites. It is "trapped" in a particular set of tunnel states by the distortion of the lattice which is centered on the octahedral site at the center of the ring. Transitions between

these tunnel states is extremely rapid and can be studied by a variety of low temperature techniques. We have applied low temperature heat capacity measurements, elastic and anelastic techniques, neutron scattering studies and Raman spectroscopy. While many questions remain to be answered, the essential nature of the tunnel states, their symmetries, their stress responses and some of their energy levels have been established. Information has also been obtained about the isotope dependence on these tunnel states which generally has been highly nonclassical.

The relation of this model to the long range diffusive motion of hydrogen is less well established. Published data for the Group V B-H systems indicates that significant deviations from the classical Arrhenius temperature dependence occurs at temperatures well above $\theta_D/2$. Our Gorsky effect measurements do not indicate any significant nonclassical behavior above $\theta_D/2$ thus raising the question of why such a disagreement occurs. Since a recent theoretical development suggests the possibility of phonon assisted tunneling from excited states as a means of understanding high temperature deviations, it is important to establish whether they are due to intrinsic lattice behavior or due to impurity effects.

Long range diffusion of hydrogen is expected to occur by phonon assisted tunneling between (100) rings which are all interconnected. The kinetics of this process should be described by the Flynn-Stoneham process or the analogous tunneling from the excited (or optic mode) states. Tunneling occurs between the occupied (100) ring in which the energies of the tunnel states are reduced by the self-trapping energy to the adjacent connected ring. This jump corresponds to an octahedral-octahedral jump of the ring center and a tetrahedral-tetrahedral jump of the H interstitial. This long range diffusion is being studied using the Gorsky Effect. These measurements have been carried out for Nb-H and Nb-O-H alloys to study the trapping effects of O interstitials and of dislocations and on the Nb-Ta alloys to study the effects of substitutional alloying. The trapping effects correlate well with the independently determined trapping parameters obtained from the high frequency measurements of trapped H described below. A particular emphasis of the Gorsky Effect studies was the isotope effect on the diffusivity. Measurements of H, D and T in Nb showed a very large nonclassical isotope effect for H and D but an almost classical effect for D and T.

To extend these studies we have studied the diffusive behavior of muons in Nb since muons may behave as a light isotope (1/6 the H mass) of H. The results of the muon studies, while of great intrinsic interest, are yet not easily related to the H diffusion behavior. It is clear, however, that the theory of the isotope effect for light interstitials is not yet complete.

We have begun to examine the mechanisms which hydrogen is transported across the gas-metal interface. These investigations are of direct interest in understanding hydrogen embrittlement failures caused by gaseous environments, as the kinetics of these failures are controlled in part by the hydrogen transfer. In these experiments we are also attempting to understand the effects of adsorbed molecular species such as H_2O , H_2S , SO_2 and O_2 on these processes. The particular molecules chosen for study are those which are known to accelerate (H_2S) or to stop (H_2O , SO_2 , O_2) hydrogen induced crack propagation.

Phase transitions in the Group V B hydrides will be investigated over the next few years. These studies are an outgrowth of our TEM measurements on niobium hydrides which discovered several phenomena such as long period superlattices, hydrogen density waves and hydrogen vacancy ordering. Our acoustic studies of the α' - β transition temperature suggest that the transition is characterized by heterophase β phase fluctuations in the α' phase. Preliminary neutron scattering results in the α' phase support the presence of these β phase heterophase fluctuations. We will be extending these investigations with particular emphasis on heterophase fluctuations, on H density waves and on long period superlattices. The techniques applied will be electron diffraction, microscopy neutron scattering and acoustic techniques. The first hydride transitions studied will be those in the Nb-H system. Hydrogen density waves are analogous to charge density waves in many of their properties. Since the basic interactions are those of elastic dipoles, the behavior of the H density waves should reflect the elastic properties of the matrix. It should therefore be possible to build modulated hydride structures using M.B.E. methods to develop a layer structure of metal pairs such as Nb and Ta or Nb and V and by controlling the hydrogen concentrations. The properties of these artificially modulated structures will be studied in addition to those of the spontaneously modulated hydrides.

TECHNICAL PROGRESS FY 1980

The general understanding of the mobility of light interstitials in bcc metals, which we have developed based upon our experiments as well as those of other investigators is:

- (a) Delocalized hydrogen at very low temperatures. Hydrogen moves in a (100) ring of tunnel states formed from the tetrahedral and triangular interstitial sites. Motion between these tunnel states is by quantum tunneling.
- (b) Motion through the lattice is by phonon assisted tunneling between the connected rings as described by the Flynn-Stoneham theory or the analogous tunneling from excited states. The interstitial self-trapping energy on a particular (100) ring results from the averaged lattice distortion centered on the octahedral site at the center of the ring.
- (c) At elevated temperatures 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. The transition temperature between classical and nonclassical behavior remains to be determined as does the significance of excited state tunneling.
- (d) Trapping occurs at interstitial solutes, dislocations and other strain centers. Hydrogen occupies (100) rings near the trapping site and motion around this site is by phonon assisted tunneling between rings.

In the past year we have continued our studies of the H diffusion mechanisms in bcc metals with emphasis on the behavior of untrapped H. We are emphasizing techniques which have a higher sensitivity to H solutes since retention of untrapped H at low temperatures is possible only at very low concentrations.

The two methods we are using are the "anelastic piezoresistance" technique and the "electron scattering induced transition" method both of which take advantage of the anisotropy of electron scattering from a defect of lower symmetry than the host lattice. In the "anelastic piezoresistance" method a periodic stress is used to cause defect reorientation in a specimen carrying a dc current. The ac potential in phase and at quadrature to the stress field carries the information about the defect reorientation kinetics. Since this ac potential can be measured with a high precision, we are able to apply this method to the explanation of very dilute solutions of H in Nb, Ta and other bcc metals. The second, somewhat analogous technique of "electron scattering induced transitions" is based on induced reorientations of the hydrogen interstitial by a high electron flux produced by extremely high ac current densities. The anisotropy of the electron scattering cross-section of the interstitial results in a net force on the interstitial whose induced reorientation appears as a nonohmic behavior. This electron induced resistance anisotropy is also expected to have a high sensitivity for interstitial hydrogen at low temperatures.

During this past year we have designed, constructed and tested the apparatus for the "anelastic piezoresistance" measurements. The accessible temperature range is 4-300 K and the frequency range is from dc to about 10 kHz. While this method has been shown to work for heavier interstitials in Nb and Ta we have not yet successfully demonstrated the effect for H. It is planned to do so shortly.

The apparatus for the "electron scattering induced transitions" has also been constructed and tested. The accessible temperature range is also 4-300 K and the frequency range is from about 10 Hz to very high frequencies which are limited only by the available electronics. This method has been extensively tested on the Nb-H system and was shown to be successful in detecting the relaxations caused by trapped hydrogen. The relaxation equations for this method have been developed. As a consequence of the relaxations due to hydrogen and the anisotropy of scattering from the hydrogens third and higher odd harmonics of the exciting frequency are developed. These have been experimentally detected and their dependence on temperature and frequency are in agreement with the theoretical expectations.

We are applying these methods to examine the validity of kinetics and crystallography of the relaxations. These measurements should yield as detailed an understanding of single H and H-H pairs as was obtained for O-H and N-H pairs.

In the past year we have begun to determine the interaction of hydrogen with metal surfaces. These studies are of direct interest in understanding hydrogen embrittlement failures from gaseous environments as the kinetics of these failures are controlled in part by hydrogen transfer across solid-gas interfaces. We are studying the kinetics of hydrogen transport across the surface of niobium and the effects of adsorbed molecular species such as H_2O , H_2S , SO_2 and O_2 of these processes. The particular molecules chosen for examination are those which are known to accelerate (H_2S) or to stop (H_2O , SO_2 , O_2) hydrogen-induced crack propagation. A combination of techniques is being applied. Permeation of H through the specimen is monitored under conditions for which the rate is controlled by surface processes while the surface composition is determined using Auger techniques. Raman spectroscopy will be used to examine

the vibrational modes of the adsorbed molecules and the effects of hydrogen adsorption on these modes. We hope to determine changes in the atomic bonding and adsorption of the molecular species when hydrogen is introduced and co-adsorbs. In addition to the effects of adsorbed species on the surface processes we will examine the effects of lattice imperfections such as dislocations and grain boundaries. Characterization of these defects will be carried out using TEM and x-ray methods.

The apparatus for carrying out these measurements has been constructed and is presently being used for hydrogen permeation studies in niobium in the temperature range 300 to 1300 K. Existing data is extremely poor, showing a large amount of scatter and even the wrong temperature dependence. Since the activation enthalpy for permeation is the sum of that for diffusion and solution from the gas phase, the value should be negative in the case of hydrogen in niobium. The permeability should increase as the temperature decreases whereas the opposite temperature dependence is reported. Our data is not yet sufficiently extensive to settle this point.

Gorsky effect measurements of hydrogen diffusion in a range of Nb-Ta alloys have been carried out to examine the effect of alloying on the reported high temperature departures from the classical Arrhenius behavior. These results, shown in Fig. 1 show the onset of high temperature curvature as Ta is added to

Nb. The data suggests that the variation of the tunneling parameters are not monotonic with composition and that they reflect the changing lattice potentials as the alloy composition is changed. These variations cannot be due to trapping effects but are consistent with the dependence of the tunneling parameters on environment determined in the O-H and N-H experiments.

RELATIONSHIP TO OTHER PROJECTS

An understanding of the phenomena discussed above has required the use of a variety of techniques, and we have worked in a collaborative mode with other groups in the MRL and at outside laboratories. This collaborative mode, while not without its difficulties, has been successful and we expect to continue it in the future. Worldwide interest in the areas we have chosen to work in is manifested by the large and well-funded research groups in Germany, France, Russia, Poland and Japan. In this country our work interfaces well with relatively large efforts at Sandia Laboratories, Oak Ridge National Laboratory and Argonne National Laboratory. By a collaborative effort with scientists at a number of institutions as well as those at Illinois, we have maintained a position at the leading edge of the field.

In addition to DOE support, we have programs in the area of hydrogen embrittlement which are supported by the ONR and NSF. The DOE program is highly interactive with the ONR and NSF efforts and yet has a distinctive character of its own. Our DOE work focusses on the mobility of hydrogen in solids with an emphasis on understanding the fundamental mechanisms involved and on the properties of and phase transitions in hydrides. The ONR program addresses the problems of hydrogen embrittlement in metals from a fundamental mechanistic point of view. Since embrittlement kinetics are largely controlled by hydrogen mobility and the fracture in many systems is due to stress induced hydride formation, the DOE program supplies the necessary fundamental understanding of these processes. The NSF program is designed to apply many of the concepts developed on the other two programs to a system of engineering importance; the Fe-Cr-Ni system with an emphasis on stainless steels. In all of these programs, we are more interested in mechanistic understanding than in simple characterization of behavior. Every attempt is made to develop predictive tools and to generalize behavior from the studies of model systems.

The capabilities developed in our laboratories for the preparation of materials and for the study of light interstitial behavior are unique. We have made many of these facilities available to other investigators as a basis for joint investigations and have occasionally supplied crystals for use in other investigations.

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.

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H. K. Birnbaum

Mechanisms of Hydrogen Diffusion in BCC Metals

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P. E. Zapp and H. K. Birnbaum

Mobility of Hydrogen Around Nitrogen and Oxygen Trapping Sites - Phonon
Assisted Tunneling Parameters

Acta Metall. (in press)

P. E. Zapp and H. K. Birnbaum

Solute Trapping of Hydrogen in Niobium: Symmetry of the O-H Pair

Acta Metall. (in press)

MRL SUPPORTED THESES (Calendar Year 1979):

Philip Emerson Zapp

Anelastic Studies of Interstitially Trapped Hydrogen in Niobium

Ph.D. thesis, Metallurgical Engineering, H. K. Birnbaum, adviser (1979)

MECHANICAL PROPERTIES OF SOLIDS

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ABSTRACT

The studies are directed toward mechanical properties of solids, primarily utilizing ultrasonic techniques and simultaneous measurements of other types. The problems being studied are from areas of solid state physics and geophysics. Our studies of dislocation motion in ice have established the nature of the large intrinsic viscous drag on free dislocation segments. They have demonstrated that the recoverable motion of dislocation segments between point obstacles is an important factor in the plastic behavior of ice, and our observations indicate that processes other than those presently considered for free segments limit this type of motion. Our study of laboratory deformation of rock is concerned with the nature of crack nucleation and growth, the interrelationship between microfracture and local plastic deformation, and the nature of the progression from initial microfracture to ultimate macroscopic fracture and failure. Our studies have provided a means for distinguishing microfracture and twinning events on the basis of acoustic emissions generated during deformations. The study of deformations in marble indicate that specific identification of intragranular and intergranular processes can be made in different regimes of deformation. A collaborative study of electron-irradiated metal-alloy systems has revealed a wealth of information concerning point-defect-impurity complex behavior in metals.

PURPOSE

The principal concern of the project are the microscopic processes important for the mechanical properties of solids. Studies are generally carried out in relatively simple systems in an attempt to better understand mechanical behavior in more complex natural systems. Measurements made by ultrasonic techniques are a principal resource. Current efforts are concentrated on dislocation dynamics in crystalline ice and deformation mechanisms in geologic systems. We also collaborate with A. V. Granato in the ongoing ultrasonic study of point defect behavior in metal-alloy system.

The objective of the studies of deformation in geologic materials is the determination of the nature and relative importance of the numerous microscopic deformation processes which contribute to the overall macro-

scopic mechanical behavior. The first step has been the development of experimental techniques to identify and monitor the contributions of various processes-particularly twinning and both ultra- and transgranular microfracture - continuously during the deformation of samples of natural materials in the laboratory. The approach being used is the simultaneous measurement of acoustic emissions in the 10 kHz - 1 MHz range, ultrasonic velocity changes, macroscopic volume change of the sample, and axial strain during the triaxial deformation of specimens in high pressure testing vessels. Measurements are often supplemented by microscopic examination of sample sections following deformation.

The general area of microfracture and its role in deformation is a topical and exciting field, with active participation from researchers in physics, geology, ceramic engineering, civil engineering, and metallurgy. In addition to its role in influencing mechanical behavior, the generation of microfractures in geologic system is very important for the characterization of petroleum reservoirs, geothermal systems, and radioactive waste storage sites. Our primary interest in this project is in the nature of crack nucleation and growth, and the progression from microfracture to the ultimate macroscopic deformation and failure. The subject is well suited for investigation using ultrasonic and acoustic emission techniques; and some of the concepts of dislocation dynamics appear to have application in the treatment of crack growth.

We have found that 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. 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 a continuous motion of these boundaries is optically observed 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 levels. The measured microstrain behavior of these samples provides direct information about dislocation velocities during the tests. The first approach has been used to investigate the interactions between dislocation segments and point obstacles at the segment ends, and the effects of HF impurities in the 1-10 ppm range on the dislocation motion. The measurements have been supplemented with internal friction measurements. The tilt boundary studies in samples with point obstacles represent the first continuous direct observation of the dynamics of pinned dislocation segments. These results set the stage for investigation in the more general area of plastic flow. Some of the results from our early studies are now being used by theoretical geophysicists in the description of mantle rheology.

The study of irradiation-produced defects in metals is a primary concern of A. V. Granato, in which this project maintains an active role. Through the

development of the high resolution velocity measurement systems necessary for this type of measurement, the ultrasonic techniques offer a new order of sensitivity and symmetry detection for the area of point defect investigations. The details of the scope and projected results of this project are described in the proposal of Professor Granato.

TECHNICAL PROGRESS FY 1980

Most Significant Results

The initial experimental rock deformation study was completed in FY80, in which analysis of acoustic emissions signals was used to distinguish and monitor specific deformation processes continuously during the laboratory deformation. Axial stress and strain, total volume change, axial velocity changes of 1 MHz longitudinal sound waves, and acoustic emission signals up to 1 MHz frequencies were all measured and recorded during the axial constant strain-rate compression of natural marble samples, which are almost pure calcite polycrystals of uniform grain size. The hydrostatic confining pressure environment of the samples was controlled and its role in suppressing microfracture and other frictional deformation mechanisms relative to twinning and other plastic mechanisms provided a means for identifying the processes generating different types of acoustic emissions.

The three distinct types of acoustic emissions which were observed, and their frequency spectra, are shown in Fig. 1. The type A signals, with a broad, poorly-defined frequency spectrum between 100 and 300 kHz, were identified as microfracture-event signals. The type B signals, which

Fig. 1. Typical acoustic emission signals (left hand side) and their corresponding frequency spectra.

occur as brief bursts of a few cycles or as long pulses such as shown, have better defined shapes and frequency spectra. Analysis of the results demonstrated that they resulted from the formation of twin lamellae. The type C signals have very poorly-defined pulse shapes but their frequency content consistently display the presence of both the type A and type B signals. Analysis of thin-sections confirmed the identification of these signals as those resulting from intragranular microfractures induced by the strain concentrations at the intersections of twin lamellae in adjacent grains.

The macroscopic deformational behavior can be subdivided into three regimes on the basis of two critical stress levels, which are functions of both the confining pressure and the grain size of the marble (Fig. 2). The yield stress, at which the stress-strain deviates from linearity, corresponds to the onset of twin-induced microfracture, as evidenced by the occurrence of type C acoustic emissions. The microfractures generated in this regime must be essentially "closed cracks" because of the absence of measurable increase

Fig. 2. Critical stress values for samples with average grain size of: (a) 0.2 mm, (b) 0.5 mm, and (c) 2 mm. Solid circles yield stress; open circles-onset of total as determined from total sample volume; open triangular - onset of dilatancy as determined from ultrasonic velocity decreases.

in the sample volume below the next critical stress level (onset of dilatency). The presence of open microcracks leads to an increase in total sample volume and a decrease of the sound wave velocity; the two values in Fig. 2 are in agreement for the higher confining pressures. Optical observations of thin sections of samples deformed to the different regimes indicate that the microfractures formed below the onset of dilatency are wholly intragranular, while cracks above this stress have propagated across one or more grain boundaries.

The overall description is consistent with expectations derived from the analogy with the simple dislocation pile-up model for crack nucleation and propagation. Namely, 1) the observed yield stresses and the onset of dilatency vary as the inverse square root of the grain size, as predicted for both the critical stress for crack nucleation and trans-granular crack propagation; 2) the yield stress is relatively independent of confining pressure, reflecting the absence of frictional effects between surfaces of closed twin-induced microfractures; and 3) the onset of dilatency is strongly pressure-dependent, as expected on the basis of the frictional forces between crack faces, which must be overcome before crack propagation can occur.

Results of this investigation were presented at the Spring Annual Meeting of the American Geophysical Union in April.

Other Results

A second rock deformation study was begun during FY80, to further explore microfracture in the simple marble systems. In preparation for these measurements and subsequent investigations of technologically important systems, a number of improvements on the experimental systems are being implemented. The data acquisition and processing systems required upgrading, and a system for ultrasonic pulse-echo attenuation measurements in the very high-loss rock samples is under development. This activity has been greatly facilitated by the expertise and experience of the current post-doctorate appointment in areas of digital electronics and ultrasonic measurements.

In the collaborative study of point defects in metal alloy systems, continued measurements have substantiated and further delineated the behavior of defect complexes in Al-Fe and Al-Zn. Measurements for the oversized-impurity Al-Mg system have begun. An automated digital control and data acquisition system is being implemented and a system for continuous velocity and attenuation measurements at two frequencies is being developed. Early results of this study were presented in three papers at the March APS meeting. Progress during FY80 is discussed in detail in the proposal of Professor Granato.

Measurements of transient creep behavior of predeformed ice crystals have been carried out, as part of the investigation of recoverable dislocation segments, begun in FY79. The formalism was largely developed for the incorporation of prismatic glide effects in the numerical analysis of the motion of pinned segments, in an effort to understand the anomalously small velocities observed experimentally in our previous research. Further progress in this project was significantly delayed by personnel turnover.

RELATIONSHIP TO OTHER PROJECTS

There is a valuable and continuing interaction of this project with that of Professor Granato. Such an interaction between faculty in the Geology and Physics Departments would be very difficult outside the interdisciplinary content of the Materials Research Laboratory.

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 applications of the present research to hydrocarbon deposits is under continuous scrutiny. Professor Donath served on an American Physical Society panel investigating radioactive waste disposal and his principal activity is still in that area. The utilization of results from our study in site evaluation and monitoring are continuously being considered.

There have an ongoing but informal interaction with Professor S. D. Brown in Ceramic Engineering, who is investigating thermal activation effects in crack propagation.

We are carrying out a measurement of elastic constant pressure dependences with Professor D. A. Payne in the Department of Ceramic Engineering. The preliminary work now underway, on synthetic crystals of the mineral enstatite which were grown on project by Dr. A. Grandin de L'Eprevier, will determine the desirability of pursuing more comprehensive studies.

PUBLICATIONS (Calendar Year 1979):

None

MRL SUPPORTED THESES (Calendar Year 1979):

Theodore Allen Koelsch

Relationship of Acoustic Emission and Ultrasonic Velocity to Deformation
Mechanisms and Dilatancy During the Ductile Deformation of Marble

Ph.D. thesis, Geology, J. T. Holder, adviser (1979)

Sekyung Lee

Limiting Mechanisms of Dislocation Motion in Ice

Ph.D. thesis, Geology, J. T. Holder, adviser (1979)

COUNCIL ON MATERIALS SCIENCE

Director: Robert J. Maurer
Professor of Physics

Supporting Agency: U. S. Department of Energy

PURPOSE

The Council on Materials Science consists of a Director and Steering Committee. Its activities are supported by Contract DE-AC02-76ER01198 of the Department of Energy with the Materials Research Laboratory of the University of Illinois.

The Director is Robert J. Maurer, Professor of Physics, University of Illinois. The members of the Steering Committee are:

Dr. Philip Anderson, Bell Laboratories

Professor Robert Balluffi, Center for Materials Science and Engineering
Massachusetts Institute of Technology

Dr. W. Dale Compton, Vice President for Research
Ford Motor Company

Dr. Brian Frost, Director, Materials Science
Argonne National Laboratory

Professor W. D. Kingery, Department of Ceramic Engineering
Massachusetts Institute of Technology

Dr. Philip Seiden, IBM Research Center

Dr. David Shirley, Professor of Chemistry
University of California at Berkeley

Dr. Dale Stein, President, Michigan Technological University

Dr. John C. Wheatley, Professor of Physics
University of California at San Diego

The purpose of the Council is to provide a channel for the input of relevant information from the active members of the materials science community to the Division of Materials Science of the Department of Energy. The Division has the difficult task of allocating limited resources for research within a critically important but broad and diverse field. The research scientists are a prime source of information concerning the status, potential value and relevance of current materials research to the Department's mission. The Council acts to focus the responsible judgment of the scientific community on issues of importance for the Division's decisions.

The Council functions by (a) identifying energy relevant materials research areas, (b) organizing panel workshops whose members are active materials scientists for the investigation of selected areas of basic research, and (c) evaluating the conclusions of the panels and consulting with the staff of the Division of Materials Science concerning the implications and relevance for the Division's mission.

A panel normally consists of approximately 15 members who meet for a period of about two weeks. The panel chairman and the panel topic are chosen by the Steering Committee in consultation with the Division's staff. Panel members are chosen by the panel chairman in consultation with the Director and Steering Committee. A Steering Committee member, designated by the Director, assumes a general advisory function for the operations of a panel.

The Council's activities also serve to focus the attention of the scientific community on the areas of materials research of specific concern to the Department of Energy. The character of truly innovative basic research is such that the initiative for novel advances is the responsibility of the research scientists, who form a closely interacting community. The long range success of the nation's energy program depends in no small measure on the interaction of this community with the Department of Energy so that both talent and resources are effectively employed on problems and opportunities.

The role of the Council is of particular importance with respect to areas of advanced innovative basic research where the judgment of informal, involved members of the scientific community is vital for assessment of the potential value and relevance of the research for energy applications.

TECHNICAL PROGRESS BY 1980

A panel on "New Materials" was chaired by Professor T. Geballe of Stanford University. A panel on "Corrosion" was co-chaired by Professors Robert Rapp and Digby Macdonald of Ohio State University.

RELATIONSHIP TO OTHER PROJECTS

The Council's activity is related to that of the National Research Council's Solid State Sciences Panel and Committee. The NRC's Panel and Committee surveys current solids state science research and, from time to time, investigates specific areas. It is not, however, primarily concerned with energy relevant research nor is it responsible to the Department of Energy for the planning or results of its activity.

KC-02-01-03 Physical Properties

INTERSTITIAL SOLID SOLUTIONS

Principal Investigator: Carl J. Altstetter
Professor of Physical Metallurgy

Supporting Agency: U. S. Department of Energy

Senior Staff: Carl J. Altstetter, Professor

Junior Staff: Roberto DeAvillez, Brazilian Atomic Energy Fellow
Jonathan D. Dobis, Research Assistant
Jen S. Lee, Research Assistant

ABSTRACT

The objective of this research is to understand the behavior of oxygen in pure metals and alloys--to determine its distribution among the metal atoms and to measure the strength of its interactions with the metal atoms. This is done by making equilibrium and kinetic emf measurements on an electrolytic cell whose electrodes differ in oxygen content. What makes this possible is the unique ability of the superionic conducting electrolyte to convert the chemical potential difference of the two electrodes into an electrical potential difference. By developing better ways to fabricate thinner electrolytic cells using vapor deposition, molecular beam epitaxy or powder processing, it is expected that measurements may be made at lower temperatures, where interactions between oxygen atoms and between oxygen and metal solute atoms, are stronger and give rise to ordering of the oxygen atoms. Measurements have been completed on niobium and niobium alloyed with vanadium, titanium, zirconium and tantalum, and metal-oxygen binding energies have been derived. Experiments with vanadium and its dilute alloys have now been designed, with the solutes chosen for their expected chemical and elastic interactions with oxygen. Systems and techniques suitable for producing thin layer electrolyte cells have been surveyed. Initial attempts will involve megacycle AC plasma sputtering of bulk yttria-doped zirconia.

PURPOSE

This research continues to be focussed on the interaction of oxygen with pure metals and alloys. Using a solid electrolytic cell technique, the equilibrium thermodynamic properties of oxygen in several refractory metals and alloys have been determined in the range 650-1250°C. The diffusivity of oxygen has also been determined, and the effect of metal solutes on oxygen diffusion in niobium and vanadium has been surveyed. Future work will expand the measuring range to lower temperatures and other systems where the thermodynamics of interstitial solute ordering and diffusion will be studied. This will be done by decreasing the thickness of the electrolyte and metal electrodes so that diffusion distances and therefore diffusion times are decreased. Vapor deposition of the components offers a possible technique for doing this. Molecular beam epitaxy will be employed for the ultimate reduction in electrolyte and electrode

thickness. The results of this research are of fundamental scientific interest in the understanding of solute-solute interactions in solids and the existence of dilute interstitial phases at low temperatures. They will also be of more technological importance to the Department of Energy. A better understanding of oxygen behavior will contribute to development of alloys which are resistant to oxidation or oxygen degradation and embrittlement. The cells themselves can be used as oxygen sensors. Given sufficiently fast and reliable response, they could serve in a variety of control functions; e.g. for monitoring and control of combustion processes or for control of oxidizing potential of fluids (Li, Na, He etc.).

TECHNICAL PROGRESS FY 1980

Most Significant Results.

Previous results in this program on oxygen diffusion in dilute niobium alloys have allowed us to determine values of metal solute-oxygen binding energies. These have now been interpreted in a very simplified way in terms of an elastic interaction and a chemical interaction. Similar correlations for vanadium based alloys suggest that there should be a weak repulsion between niobium solutes and oxygen. If this is true the diffusivity of oxygen should not be appreciably different in a dilute vanadium-niobium alloy than in pure vanadium. Figure 1 demonstrates that this is, in fact, the case.

Fig. 1. Diffusion co-efficient of oxygen in pure niobium, pure vanadium and in dilute alloys.

It illustrates the marked difference between the niobium based and vanadium based alloys. The principal effect is determined by the atomic size and whether the solute atom acts as if it is smaller than the solvent atom (V in Nb) or larger than the solvent atom (Nb in V). The former system

is one showing an attractive interaction and decreased diffusion rate and the latter system, one of repulsive interaction with oxygen, and little change in diffusivity due to oxygen-solute interaction.

RELATIONSHIP TO OTHER PROJECTS

Close cooperation is maintained with Professors H. K. Birnbaum and C. A. Wert, who are also interested in solute interactions in solid solutions. Work on environmental and solid solution effects of hydrogen is also being carried on under the direction of the Principal Investigator. Cooperative arrangements have been made with Professor J. E. Greene for production of thin film electrolytic cells. The central facilities of MRL provide a focal point for interaction, particularly the electron microscopy, Auger analysis and MBE facilities. Close contact is maintained with Professors D. Peterson and N. Carlson of the Ames Laboratory and discussions are underway for joint research with Drs. B. Loomis of Argonne National Laboratory and P. Tortorelli of Oak Ridge National Laboratory.

PUBLICATIONS (Calendar Year 1979):

R. Lauf and C. Altstetter

Diffusion and Trapping of Oxygen in Refractory Metal Alloys
Acta Metall. 27, 1159-1163 (1979)

D. Shah and C. Altstetter

Prediction of Work Hardening Rate in BCC Alloys with a Dispersed
Second Phase

New Developments and Applications in Composites, D. Wilsdorf, ed.
(AIME, Warrendale, PA, 1979)

G. Steckel and C. Altstetter

Modeling of Interstitial Solute Behavior in a Body-Centered Cubic Metal
Acta Metall. 27, 1271-1279 (1979)

P. Tortorelli and C. Altstetter

Sputtering of Two-Phase Polycrystalline Metals
J. Vac. Sci. Technol. 16, 804-807 (1979)

DEVITRIFICATION BEHAVIOR IN METAL-CONTAINING SILICATE AND BOROSILICATE GLASSES

Principal Investigator: Haydn H. Chen
Assistant Professor of Metallurgical Engineering

Supporting Agency: U. S. Department of Energy

Senior Staff: Haydn H. Chen, Assistant Professor

Junior Staff: John H. Kessler, Research Assistant
Jong-Wan Park, Research Assistant

The objective of this research is to obtain a fundamental understanding of thermally induced devitrification behavior in silicate and borosilicate glasses containing fission products. This information is needed before the materials can become useful for high-level radioactive waste storage. It is generally recognized that the quality of the glass product will be affected by its thermal and radiation history. Any changes from a "homogeneous" glass can affect dispersibility of the fission products and thereby endanger the environment. As assessment of thermal stability of waste glass is thus necessary.

Silicate and borosilicate glasses are widely used glass formers because of their remarkably high solubility for numerous metal oxides. Iron (III) oxide (Fe_2O_3) and molybdenum (VI) oxide (MoO_3) are being added to the alkaline-silicate and borosilicate glass, respectively, and the devitrification behavior due to thermal treatment is then investigated. The work can be divided into two major parts, (i) bonding characteristics of metal ions in vitreous glass, and (ii) nucleation and growth kinetics of devitrifying glass and its associated microstructural and compositional changes. Techniques used include extended x-ray absorption fine structure (EXAFS), infrared absorption spectroscopy, x-ray diffraction using monochromatic radiation, small angle x-ray scattering (SAXS), and scanning transmission electron microscopy. These techniques are chosen because each gives a unique information about the local atomic arrangements and microstructural changes of various stages of the thermally induced devitrification process.

PURPOSE

The goal of this research project is to obtain a fundamental understanding of the devitrification kinetics in selected glasses containing fission products. The information is needed if these materials are to become useful for high level radioactive waste storage. These fission product solutions have been stored primarily in stainless steel tanks. However, considerable interest has recently centered on use of glassy storage materials owing to their remarkably high solubility for numerous kind of metal oxides. This universality is particularly important for nuclear waste disposal, since many active nuclear species with great variation in atomic number and chemistry must be stored.

In dealing with an amorphous system, it is necessary to understand the basic atomic configuration around every glass constituent. Additionally, the development of nuclear waste storage glasses also requires both the devitrification and leaching rate to be slow so that radioactive contents may be safely stored for a long period of time without leakage. This research is therefore focused on two major subjects: First, the bonding characteristics of metal ions in the glassy state, and second, the nucleation and growth kinetics during devitrification process and its associated microstructural and compositional changes.

Silicates are the most stable glasses and therefore have been chosen as the basic glass former. In order to simplify the mechanism involved in the devitrification process, ternary glass systems are to be investigated first. The sodium disilicate glass system containing various amounts of Fe_2O_3 , $[(\text{Na}_2\text{O} \cdot 2\text{SiO}_2)_{1-x} (\text{Fe}_2\text{O}_3)_x]$ with $x < 0.3$, is one type of the glasses being studied. This is chosen because its phase diagram is well established such that its miscibility limit is known, and also because the near-neighbor geometrics around Fe, Si and Na in the vitreous state have recently been investigated. Another system based on sodium borosilicate glass containing MoO_3 is also being studied. The solubility of molybdenum in the glass is normally very low, and segregation of molybdenum-rich crystalline phases at the surface has been observed recently. This phase was found to contain not only molybdenum but also noticeable amounts of cesium and strontium. Both Cs and Sr are known to be biologically important species because of their prolonged radioactivity decay time, and their ability to be absorbed by the human body.

Several different experimental methods are used or planned for use in this research. The extended x-ray absorption fine structure (EXAFS) method is used to examine the local atomic environment of metal ions in the amorphous state, and also to monitor the local geometrical change during the very initial stage of the nucleation process. This technique is used because it can successfully provide information concerning the local atomic arrangement of a selected specie in a complicated glass matrix within a distance of approximately 8 Å. As the nuclei grow bigger, the small angle x-ray scattering (SAXS) technique can then be used to follow the kinetics of particle growth rate. This method is ideally suited to measurements of particle growth with sizes in between 10 Å and 1000 Å. Finally, when particles grow ever larger, the scanning transmission electron microscope and regular x-ray powder diffraction utilizing monochromatic x-ray beam can be employed to determine the shape, composition and distribution of these recrystallized particles embedded in the glass matrix. Infrared absorption spectrometry is also used to study the vibrational spectra of the glasses, both in the amorphous state and in the devitrified state. Apparatus necessary for the various x-ray measurements has recently been developed in the MRL x-ray central facility and in the Department of Metallurgy and Mining Engineering by the principal investigator. The STEM work is carried out by means of equipment available in the MRL microstructural facility. The infrared absorption measurement is obtained with a Bechman 4250 spectrometer available in the polymer characterization laboratory, Department of Metallurgy and Mining Engineering.

TECHNICAL PROGRESS FY 1980

Most Significant Results

(a) Bonding of Iron Oxides in Sodium Silicate Glass

Since this project began in October 1979, the necessary development of apparatus in the area of EXAFS and SAXS has been completed. High temperature vertical furnaces for glass preparation have also been established. We are not able to prepare both bulk and thin film glasses of various compositions.

All melting of glasses is done in air in recrystallized Al_2O_3 (or platinum) crucibles at temperatures as high as $1400^\circ C$, using a vertical globar furnace equipped with a specially designed elevating device for specimen transportation. Thin glass films of less than $10 \mu m$ thick, necessary for infrared absorption measurements, are prepared by blowing techniques. Films of $50-100 \mu m$ thickness, necessary for SAXS measurements are made by diamond-saw slicing and subsequent mechanical polishing and chemical etching.

The first task of our work has been to understand the bonding geometrics of iron ions in sodium silicate glasses. This we are approaching in the following manner:

(1) K-Absorption Edge Shift

The shifts of x-ray absorption edges of an element in different compounds depend upon factors such as the valency, degree of ionicity and coordination numbers. The chemical shift is toward the high-energy side of the metal edge and it increases progressively with an increase in the valency of the cation, unless the shift is either suppressed by the covalent character of the bond or enhanced by the formation of metal-metal bonding. This characteristic is best described by a term called effective coordination charge, η_K , and is defined as

$$\eta_K = Z - f_c n$$

where Z is the valence, f_c is the degree of covalence of the given bonds ($f_c = 1 - f_i$ where f_i is the degree of ionicity), and n is the coordination number.

The term, η_K , of an element in different forms of compounds, is generally found to be linear with the K-edge shift of this element. Measurements of K-absorption edge shifts of Fe in various compounds including $Fe_{0.885}O$, $Fe_{0.905}O$, Fe_3O_4 , Fe_2O_3 , Fe metal, $Fe_{36}Cr_{32}Ni_{14}P_{12}B_6$ metaglass, and $[Na_2O \cdot 2SiO_2]_{0.8}[Fe_2O_3]_{0.2}$ oxide glass, were performed in our laboratory. A linear relationship between the K-edge shifts and η_K is observed (Fig. 1).

Fig. 1. Variation of the shift of the K-absorption edge for Fe with the effective coordination charge: (1) $Fe_{0.885}O$ and $Fe_{0.905}O$; (2) Fe_3O_4 ; (3) Fe_2O_3 and $[Na_2O \cdot 2SiO_2]_{0.8}[Fe_2O_3]_{0.2}$; (4) $Fe_{36}Cr_{32}Ni_{14}P_{12}B_6$ when plotted on the same curve to obtain η_K .

In fact, the edge position of iron in iron-sodium-disilicate glass is identical to that in Fe_2O_3 , suggesting that the ionic status and geometrical coordination of trivalent iron in sodium-disilicate glass shows great similarity to the trivalent iron in Fe_2O_3 crystal.

(2) Infrared Absorption Spectroscopy

In order to further understand the local atomic arrangements around iron in the sodium-disilicate glass system, the vibration modes of iron glasses with the presence of various amounts of Fe_2O_3 were investigated by means of the infrared absorption spectrometry. We have obtained IR spectra for three different sodium-disilicate glasses containing 5, 10 and 20 mole percents of Fe_2O_3 (Fig. 2).

Fig. 2. The IR absorption spectra for three iron glasses (1) $(\text{Na}_2\text{O} \cdot 2\text{SiO}_2)_{0.95}(\text{Fe}_2\text{O}_3)_{0.05}$, (2) $(\text{Na}_2\text{O} \cdot 2\text{SiO}_2)_{0.9}(\text{Fe}_2\text{O}_3)_{0.1}$ and (3) $(\text{Na}_2\text{O} \cdot 2\text{SiO}_2)_{0.8}(\text{Fe}_2\text{O}_3)_{0.2}$. The superimposed dotted lines refer to the IR spectra of a pure sodium-disilicate glass.

When superimposed upon that of a pure sodium-disilicate glass (dotted lines), two features are noticeable: (i) all three iron glasses show great similarity in the general shape of their absorption spectra, and no obvious new band is observed when compared to the infrared absorption spectrum of a pure sodium-disilicate glass; and (ii) for the 5 mole percent iron glass, the position of each absorption band appears to be identical to that of a pure sodium-disilicate glass, but a general shift of bands toward the lower wave-numbers is seen for the other two iron glasses.

These observations can be understood if following picture is postulated. We have concluded from previous absorption edge measurements that coordination geometry of iron in the amorphous glass is similar to that in Fe_2O_3 , indicating the existence of $(\text{Fe}-\text{O}^-)$ bond. It is also well established that the IR spectrum of sodium-disilicate glass consists of (i) the antisymmetric stretching mode of bridged oxygens (i.e. $\text{Si}-\text{O}-\text{Si}$ bond) at 1050 cm^{-1} , (ii) the stretching modes of nonbridged oxygens (i.e. $\text{Si}-\text{O}^-$ bond) at 950 cm^{-1} , (iii) a linked $\text{Si}-\text{O}-\text{Si}$ symmetrical stretching mode at 760 cm^{-1} , and (iv) two other bands near 600 cm^{-1} and 760 cm^{-1} related to the doubly degenerated and triply degenerated bending modes involving bridged oxygens. Combining these information in conjunction with our present experimental information, it can be concluded that the dissolution of Fe_2O_3 into sodium-disilicate glass causes some of the original bridged and nonbridged bonds to be disrupted. The absence of any new bands in these iron glasses as well as the great similarity between these iron glasses and sodium-disilicate glass indicates the nature of bonding around Fe shall be one (or both) of the following types, (i) $\text{Fe}-\text{O}^-$ and (ii) $\text{Fe}-\text{O}-\text{Si}$. With this concept in mind, we would expect the infrared spectrum to show the original features of a pure sodium-disilicate system when the concentration of Fe_2O_3 is small first because the percentage of new bonding ($\text{Fe}-\text{O}-\text{Si}$) is small in this case and second because the ratio between the bridging and nonbridging oxygens would remain unchanged. When the concentration of Fe_2O_3 increases, since the ionic bonding between oxygen and iron is weaker than the partially covalent bonding between oxygen and silicon, a shift of the IR absorption bands toward lower wave numbers would be expected. Both of these aspects of behavior are actually present in our IR data which thus supports our proposed model.

(3) EXAFS and X-ray Photoemission Spectroscopy (XPS)

Perhaps the most convincing information concerning the bonding characteristics of trivalent iron in the glass is obtained from the direct structural determination of the EXAFS measurement together with the XPS method which examines the charges of electronic structures of glass constituents. These studies were carried out in collaboration with Dr. D. J. Lam, B. W. Veal and G. S. Knapp of Argonne National Laboratory. Results of these two experiments confirm the bonding geometrics of iron in sodium silicate glass. There are six oxygens surrounding an iron ion, of which only three of them are actually bonded to iron with a distance of $1.85\text{ \AA}$, the other three are located at slightly longer distances from iron in a geometry similar to that in Fe_2O_3 crystals. Both the bridging and nonbridging oxygen atoms existing in the original sodium silicate glass matrix are utilized in order to form this new structure when iron oxides are dissolved in. The amount of disrupted bridging and nonbridging oxygens is actually proportional to the initial concentration of each type of oxygen bonds existing in the glass before Fe_2O_3 is added.

(b) Crystallization in Iron-Sodium-Disilicate Glass

The second task of this work is to study the nucleation and growth kinetics during the devitrification process. We have performed IR measurements on glass thin films after annealing them at various temperatures for different period of time. The heat treatment of a 20 mole percent iron glass at 515°C for 72 hours did not show any appreciative change of the IR spectrum. (apparently the driving force for the crystallization is rather weak at this temperature). After annealing at higher temperature (550°C) for an hour there is already a new IR absorption band developed at 610 cm^{-1} wavenumber. This band subsequently increases in magnitude with increasing annealing time. On annealing the same glass at an even higher temperature (580°C) one finds a remarkable growth of this extra IR band, although the remaining bands remain unchanged. Figure 3 shows these IR spectral changes at three annealing temperatures. The appearance and growth of the IR absorption band at 610 cm^{-1} suggests the possibility that some kind of microstructural changes occur. Scanning electron micrographs were therefore taken on those annealed glass films.

Fig. 3. Comparison of the IR absorption spectra for a 20 mole percent iron glass taken after: (1) 17 hour annealing at 515°C, (2) 24 hour annealing at 550°C and (c) 24 hour annealing at 580°C.

RELATIONSHIP TO OTHER PROJECTS

In the course of studying the bonding characteristics of metal oxides in glasses, results from x-ray photoemission spectroscopy are important to the final conclusions achieved. The XPS experiments are being carried out by Drs. D. J. Lam and B. W. Veal of Argonne National Laboratory.

At the University of Illinois, an interdisciplinary group with mutual interests in the area of glass crystallization research has recently been formed. Group members include Professors C. G. Bergeron, S. D. Brown, and S. H. Risbud of the Department of Ceramic Engineering, Professor J. Kirkpatrick of the Department of Geology, and the Principal Investigator. Valuable discussions and sharing of research equipment are among the activities of the group.

Developments of EXAFS, SAXS and x-ray diffraction equipment necessary for this research are made possible through the MRL x-ray central facility. This equipment serves as the primary research tool for the writer.

PUBLICATIONS (Calendar Year 1979):

H. Chen

X-Ray Absorption Study of Effective Coordination Charges of Iron
in Crystals and Amorphous Solids
J. Phys. Chem. Solids (submitted to)

H. Chen and J. B. Cohen

Pretransition Phenomena in First-Order Order-Disorder Transitions
Metall. Trans. A (submitted to)

H. Chen and J. W. Park

Surface Reaction of Sodium-Disilicate Glasses
Acta Metall. (submitted to)

J. W. Park and H. Chen

An Infrared Study of Crystallization in Sodium-Disilicate Glasses
Containing Iron Oxides
J. Noncrystalline Solids (submitted to)

DIELECTRIC SOLIDS

Principal Investigator: David A. Payne
Associate Professor of Ceramic Engineering

Supporting Agency: U. S. Department of Energy

Senior Staff: David A. Payne, Associate Professor
Alain Grandin de L'Eprevier, Vis. Res. Assistant Professor

Junior Staff: John U. Knickerbocker, Research Assistant
Bruce A. Tuttle, Research Assistant

ABSTRACT

The dielectric solids research program is concerned with the synthesis, preparation, crystal growth, fabrication, characterization and property measurements on new and improved polar materials for energy conversion and detection systems. Materials under investigation include Bi_2WO_6 , an anisotropic layered compound for piezoelectric applications. Crystals are grown from Na_2WO_4 -NaF fluxes, and polycrystalline samples densified by hot-forming methods. Other crystals grown include Bi_2NbO_6 , $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{Ca}_2\text{V}_2\text{O}_7$ and $(\text{Na,Bi})(\text{MoO}_4)_2$. Polycrystalline ceramics of $\text{Pb}(\text{Zr,Sn,Ti})\text{O}_3$ are sintered in controlled atmospheres of lead oxide. Ferroelectric measurements are concerned with field enforceable antiferroelectric switching. Parameters of interest are spontaneous polarization, switching time and electrocaloric cooling. A central theme of the project is the interrelationships that exist between processing and properties for ceramic materials. The internal boundary conditions within electrical ceramics are of special interest, and are characterized by a variety of techniques, including STEM and Auger analysis.

PURPOSE

The dielectric solids research program is concerned with synthesis, preparation, crystal growth, fabrication, characterization and property measurements on new and improved ceramic materials for energy conversion and detection systems. A central theme of this project is the interrelationships that exist between processing and properties for ceramic materials. Of particular interest are structure-property relations in polar materials, especially with respect to modeling polycrystalline properties on single crystal values. The role of internal electrical and mechanical boundary conditions on the dielectric performance of polarizable deformable ceramics is emphasized. Purposeful manipulation of internal boundary conditions by "microstructural engineering" techniques of (i) liquid phase sintering, (ii) chemical counter diffusion and (iii) hot forming methods, have given rise to (i) permittivity control with electric field splitting in $\text{BaTiO}_3\text{-Pb}_5(\text{Ge,Si})_3\text{O}_{11}$ diphasic ferroelectric mixtures, (ii) resistivity control with enhanced space-charge polarization in $n\text{-SrTiO}_3/p\text{-Cu}_2\text{O}$ mixtures, and (iii) mechanical orientation of ceramic microstructures in piezoelectric layered compounds. This basic work has aided in the practical development of (i) unsaturable high field ferroelectric devices, (ii) high apparent dielectric constant ($\bar{K}' \sim 10^5$) internal boundary

layer capacitors and (iii) ceramic piezoelectrics with complete microstructure orientation.

With respect to energy related applications, piezoelectrics are 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 the storage of electric energy. Materials currently being investigated include: (i) Bi_2WO_6 and Bi_2MoO_6 , anisotropic layered polar compounds which, from crystallographic calculations, should be highly piezoelectric, if only single crystals and orientated ceramic microstructures can be formed; (ii) high permittivity dielectric mixtures ($\text{BaTiO}_3\text{-Pb}_5(\text{Ge,Si})_3\text{O}_{11}$, $\text{n-SrTiO}_3|\text{p-Cu}_2\text{O}$) for energy storage, (iii) field induced ferroelectric-antiferroelectric transitions in $(\text{Pb,Sr})(\text{Zr,Ti,Sn})\text{O}_3$ and associated electrocaloric cooling for the extraction of thermal energy and direct conversion into electricity and (iv) semiconducting perovskites (of donor doped SrTiO_3 , BaTiO_3) for thermal sensors, current limiters and electrodes for the spontaneous photoassisted electrolysis of water into H_2 and O_2 fuel and chemical energy storage.

The long term program concentrates on ceramic materials for energy applications through the choice of new materials and considerations of potential material limitations. Examples include: (i) dielectric power conversion of waste heat into electricity using ferroelectric solid state heat engines (based on pyroelectric discharge and electrocaloric cooling), (ii) photoassisted electrolysis of water at semiconducting SrTiO_3 based electrodes, (iii) perovskite electrodes for MHD applications (and suppression of electrochemical degradation processes), (iv) titanate fixation of nuclear waste, (v) improved ceramic transducing devices and (vi) micro-analytical characterization of boundary conditions in polycrystalline electrical ceramics.

TECHNICAL PROGRESS FY 1980

Most Significant Results

The most significant accomplishments were in the areas of materials preparation, fabrication and equipment development. Considerable effort was expended in developing a facility for the mechanical orientation of ceramic microstructures. Three hydraulic presses, die assemblies and furnaces were designed and built, capable of hot forming in air at 1150°C and 150 MPa. Techniques employed in the orientation of layered structures include hot pressing, hot forging and hot extrusion. Several pieces of unique equipment were especially developed, including fixtures for the measurement of piezoelectric properties as a function of temperature and voltage. The most significant pieces of new equipment were (i) a calorimeter for electrocaloric measurements and (ii) micro manipulators for capacitance-voltage measurements of grain and grain boundary regions. These enable us to investigate (i) field enforced anti-ferroelectric-ferroelectric transitions and (ii) electrical boundary conditions within polycrystalline ceramics.

Last year we reported on the growth of Bi_2WO_6 crystals from $\text{Na}_2\text{WO}_4\text{-NaF}$ fluxes. Since that time we have optimized crystal growth parameters, which are now

published. 10 x 6 x 0.8 mm single crystal platelets are routinely grown, with lamellae limited by the size of the crucible. The bigger the crucible, the larger the surface area of the crystal! Thickness is developed by poisoning the rate of lateral growth by fluoride additions, and the upper limit of NaF compatibility (without Bi_2WO_6 destabilization) has been found to be 40 mole% (Figure 1). A most unusual phenomena

was observed, in that crystals grew in an orderly manner in vertical planes within the bulk of the flux! The effect of electromagnetic fields on crystal growth of high transition temperature ferroelectric materials in coil wound furnaces is being considered.

Another ferroic material being grown in $\text{Ca}_2\text{V}_2\text{O}_7$ in 7 x 5 x 4 mm size crystals. The availability of this compound has initiated two programs of research with other groups on electric and structure characterization. Preliminary measurements indicate a superstructure within the compound. The phase CaV_2O_6 is not stable under our experimental growth conditions.

FIGURE 1. THICKNESS OF SINGLE CRYSTAL Bi_2WO_6 LAMELLAE AS A FUNCTION OF NaF CONCENTRATION.

Large crystals of $(\text{Na},\text{Bi})(\text{MoO}_4)_2$ are being grown for acousto-optic purposes.

The compound is tetragonal and belongs to the CaWO_4 family of materials. The melting point is around 850°C, and large crystals exceeding 2 x 1 x 1 cm are readily obtained. Those pulled from the melt are a light yellow color, whereas those grown from the flux (LiNaMoO_4) are colorless. Spectrographic analysis indicates a Li concentration less than 50 ppm in the latter.

Polycrystalline Bi_2WO_6 can now be hot formed to theoretical density with an orientated microstructure if the precursor powder has a platelet morphology (Figure 2). The powder is initially prepared by flux synthesis or melt recrystallization. Based upon (00 ℓ) x-ray reflections, it has been shown that hot pressed samples have up to 75% orientation of the C axis along the

FIGURE 2. OPTICAL PHOTOMICROGRAPH OF HOT PRESSED Bi_2WO_6 ILLUSTRATING THE ALIGNMENT OF A PLATE-LIKE MICROSTRUCTURE.

direction, whereas hot-forged samples have greater than 95%. Other layered compounds being hot-formed, include Bi_2MoO_6 , $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{PbBi}_2\text{Nb}_2\text{O}_9$, and $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$. Pseudo single crystal symmetry was also obtained in ceramic-polymer composites, in which Bi_2WO_6 platelets were rheologically cast in elastomers to develop a well defined orientation. This should give rise to "hard" piezoelectrics with improved voltage stability.

Basic measurements on field enforced antiferroelectric-ferroelectric transitions were initiated in FY 1980. The system of interest is the $\text{Pb}(\text{ZrSnTi})\text{O}_3$ family of materials (PZST), and work concentrated on hysteresis measurements, electrocaloric coefficients, and polarization reversal switching times. The aim of the work is to investigate the effect of ceramic microstructures on stress induced polarization, secondary electrocaloric effects and domain nucleation and growth processes in polycrystalline ferroelectrics. Several compositional series of samples were prepared by sintering in a controlled partial pressure of lead oxide. Figure 3 illustrates typical results for a 50/45/5 composition. The uncompensated hysteresis loops and associated electrocaloric effects are at 60° and 80°C . One aspect of the work is to maximize the electrocaloric effect through microstructure manipulation. Work is presently proceeding along these lines.

FIGURE 3. THE ELECTROCALORIC EFFECT FOR POLARIZATION REVERSAL FOR $\text{Pb}(\text{Zr},\text{Sn},\text{Ti})\text{O}_3$ 50/45/5 AT 10^{-2} Hz AND 60 AND 80°C .

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 determination of layered compounds. Collaboration has been with the Center for Energy and Environment of the Department of Energy at the University of Puerto Rico with Professor F. Diaz-Colon. Under separate DOE contract, ER-78-S-02-4679, we are working with Power Conversion Technology, Inc., of LaJolla, California, on the evaluation of Ferroelectric Ceramics for Dielectric Power Conversion. This is a one year non-renewable project funded at \$103,784. An important aspect of the findings of the basic research carried out under this contract is their application to more applied projects in the Department of Ceramic Engineering which are receiving increasing Government, Industrial and International attention e.g. by ONR, Hughes, Ferro-Transelco, Phillips, Siemens, NPL New Delhi and Defence Academy Tokyo. Ferro-Transelco is funding a project on Strontium Titanate Ceramics for Capacitor Materials at \$60,000/year.

PUBLICATIONS (Calendar Year 1979):

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Minneapolis, MN, June 12-15, 1979
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Ferroelectric Materials for Dielectric Power Conversion
Proceedings of the International Symposium on Application of Ferroelectrics,
Minneapolis, MN, June 12-15, 1979

STRUCTURE, CRACKING AND CHEMISTRY OF CERAMIC GRAIN AND PHASE BOUNDARIES

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Supporting Agency: U. S. Department of Energy

Senior Staff: Sherman D. Brown, Professor
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ABSTRACT

This project explores the chemical and physical nature of grain boundaries and phase boundaries in ceramic materials and examines their effects on chemical and mechanical properties. Research has been focused principally on the covalently bonded materials, SiC and Si₃N₄ with two categories of objectives: 1) to examine the high temperature phase stability and crystal structures of large single SiC crystals containing small additions of impurities (Al, O, N, B, etc.) with the intention of relating these results to the structure of grain boundary regions consisting of segregated layers of impurities; 2) to examine the effects of intergranular liquid or glassy phases on the high temperature strength of Si₃N₄. Here, non-Newtonian deformation characteristics of the secondary phases are expected to control crack propagation during fracture. The phenomena associated with this behavior and the conditions under which they will occur are to be identified.

In the area of ionic materials certain basic experiments concerning MgO(+Sc₂O₃), NiO(+Li₂O) and Al₂O₃ (w/glassy grain boundaries) are also being undertaken. The latter material is of interest for high temperature fracture analysis and the former two for the chemistry of grain boundaries.

Ultimately, the information is intended to improve our ability to synthesize and fabricate dense polycrystalline ceramic materials with desirable predetermined properties.

PURPOSE

The purpose of the proposed research is to explore the influence of grain boundaries on the physical properties and fabrication characteristics of polycrystalline ceramic materials. Specifically, the mechanical strength is affected by the existence of secondary phases contained in the grain boundary. In many cases these phases are glassy, as in silicon carbide and impure aluminum oxide. Fracture tests on Al₂O₃ containing minor amounts of SiO₂ have shown that the strength decreases sharply at some elevated temperature

which corresponds roughly to the melting point or glass transition point of a typical silicate glass. Similar results have been reported for other high-temperature ceramics such as Si_3N_4 and SiC . The mechanism of fracture also changes: failure is not associated strictly with crack propagation through a homogeneous deformable solid. Detailed information about the composition of the phases and the fracture mechanism is needed to develop a predictive model incorporating the glass-like nature of these intergranular phases.

The structural characteristics of ceramic grain boundaries touch on several energy related materials problems. Silicon carbide, silicon nitride and aluminum oxide are expected to play important roles in high temperature gas turbines and coal gasifiers. SiC has also been considered as an electrode for MHD generators. The effectiveness of these materials in operations under harsh environments depends on the condition of the grain boundaries. The presence of residual secondary phases usually manifests itself at granular interfaces. These are generally recognized as being amorphous or glassy but unfortunately are not well characterized in terms of composition or properties. Excessive corrosion of these materials, when in contact with a molten salt or silicate, is caused by preferential attack and penetration at grain boundaries containing glassy or liquid phases. The unseating and removal of whole grains occurs, in addition to the other processes of oxidation and dissolution. The high temperature strength, creep resistance, and impact resistance are affected by the viscosity of intergranular phases. Consequently, a thorough understanding of, for example, silicon carbide in adverse conditions must include an analysis of the compositions of these phases. This research will be conducted on dense specimens prepared by a variety of methods. The results should lead to improved fabrication methods and applications.

Another material of some importance is lithiated nickel oxide, which has been considered as an electrode material for molten salt and acid fuel cells. Rough correlations are observed between its electrical characteristics, corrosion resistance, mechanical strength and the amount of Li_2O found at the grain boundaries, either in the form of precipitates or as segregated layers in solution. To date, the most extensive study of segregation in this system used various wet chemical methods on quenched specimens. We propose to employ Auger, SIMS and STEM methods to obtain a more accurate and systematic microscopic description of the processes that occur in the grain boundaries of this material. The information will be of major value in any future understanding of the defect structure and the electrical and mechanical behavior.

A part of our research related to grain boundary problems in ionic materials has taken the form of a cooperative program with the research efforts conducted by W. D. Kingery and A. F. Henriksen at M.I.T. Mutual interests are concerned with O^{18} diffusion in Sc_2O_3 doped MgO . Scandia has been observed to segregate preferentially at external surfaces and grain boundaries. The defect chemistry is modified, together with the ionic transport behavior at grain boundaries and surfaces. This is of intrinsic interest in relation to grain boundary motion and ionic channelling and sintering.

The proposed research bears on problems associated with the stressing and failure of rock at all levels in the earth's crust. Rocks are almost always structurally and chemically complex, and it is usually difficult to isolate the various parameters which control fracture. A simple ceramic oxide is like an idealized rock, and it is expected that strong common interests will be shared with Professor J. T. Holder's research onto the mechanical properties of geological materials. Equally strong ties will exist to the studies by Professor D. A. Payne of grain boundary doping to produce np junctions for tailored dielectric properties in acentric ceramics. The proposed work will also profit by interaction with the investigations by Professor W. S. Williams of grain boundary processes in cemented carbides.

A central asset to the proposed research is the accessibility of preeminent equipment for microscale characterization of ceramics available in the MRL central facilities. Without this instrumentation, and the expert technical personnel that maintain it, the research proposed here would not be possible. We have in mind particularly the use of the new Cameca ion probe recently installed in MRL. This instrument offers detailed chemical analyses by SIMS of grain boundary structure at a chemical sensitivity of 1 in 10^6 and submicron resolution ($\sim 3000 \text{ \AA}$). Individual grain boundaries can thereby be characterized, and the composition measured on a $50 \text{ \AA}$ scale by depth profiling into the grain. Accessories for operation at high temperatures are planned for this instrument. Transmission microscopy investigations using the HB5 STEM unit and sample thinning methods developed by Professor W. S. Williams are expected to yield chemical information on a $30 \text{ \AA}$ scale for fine grain boundaries.

It appears possible that even the surface composition of the crack tip can be probed on a $300 \text{ \AA}$ scale using a high resolution scanning Auger unit due for delivery in October 1980. The modern capabilities offer a new order of analytical exploration of grain boundary phenomena in the important ceramic materials proposed here for investigation.

Two principal areas of research activity will be as follows:

1. Compositional and Structural Characterization of Ceramic Grain Boundaries and Surfaces

This segment of the research program pursues the quantitative or semiquantitative determinations of (a) compositions of secondary phases appearing at grain boundaries, and of (b) the compositions and effective thicknesses of segregated solute layers at surfaces and interfaces and, as is the case for SiC, their effect on the local crystal structure. The results will be related to information on grain growth, sintering, grain boundary and surface diffusion and electrical properties.

Emphasis is placed on determining solute distributions and phase compositions present at the high temperatures at which ceramics are used and fabricated. Where possible, direct measurements are to be made on specimens at elevated temperatures to complement measurements on quenched specimens. A primary objective is to analyze the extent of solute segregation and precipitation for various rates of cooling. This is necessary in as much as the solute distributions in quenched specimens are likely to be different from the

characteristics maintained at high temperatures. A scanning ion microprobe, a scanning Auger and a scanning transmission electron microscope will provide the methods of direct observation. The first will be equipped with a hot stage capable of reaching temperatures in excess of 1500°C. The feasibility of a similar adaptation of the other two experimental units is presently being considered. Other, coarser, methods of measurement include surface etching by thermal and chemical techniques and coulometric titration.

2. Crack Propagation in Polycrystalline Ceramics at High Temperatures

Subcritical cracking processes in polycrystalline ceramics limit the usefulness of these materials in high temperature operation. The principal failure mechanism is intergranular cracking through the glassy grain boundaries which, at high operating temperatures, are often liquid. Cracking involves both grain boundary sliding and cavitation in the glass. This part of the research is concerned with three particular ceramic materials: Al_2O_3 , SiC and Si_3N_4 . The research proposed here is to: (a) Determine the rate of crack propagation of these materials at temperatures between 100 to 1800°C with controllable parameters including grain size and impurity concentration; (b) measure the relevant physical properties (viscosity, density, etc.) of secondary phases appearing at grain boundaries with compositions that are to be determined in other parts of this program; (c) Refine an existing predictive theory of cracking in ceramic materials by the incorporation of the observed behavior of the intergranular phases.

Facilities for the study of crack propagation at high temperatures are already largely available, using double torsion and four-point flexure methods that are well adapted to temperatures up to 1800°C. Crack propagation will be examined in various atmospheres as a function of temperature and applied stress. Acoustic microscopy equipment will be used for coarse examination of fracture surface and near-surface regions left in the wake of the crack.

The high resolution microanalytical techniques mentioned above will be used to characterize the structural and chemical nature of crack tips and surfaces. Post mortem examinations of crack surfaces after failure will give information concerning the mode of fracture (intergranular or transgranular). The role of intergranular phases and segregated impurity layers will be important particularly at high temperatures and with fine grained materials. Actual crack tips can be examined by arresting the slow crack growth process and quenching. The shape of the crack tip and the distribution of impurities and glassy phases around the tip is of primary interest. It is very likely that these characteristics control the velocity of the crack in some as yet unknown manner.

With the composition of the intergranular glass established it will then be possible to make bulk samples of the glass and so determine its physical properties as functions of temperature. The viscosity (when molten), hardness (when solid), density, surface tension (when molten), and heat of vaporization are the properties most relevant to crack propagation. These properties will be introduced into current rate theories of cracking in ceramics in an effort to synthesize a wholly predictive theory of the failure process.

The measurements will be made on both commercially and locally fabricated polycrystalline specimens. An appropriate effort to modify the failure mechanism and develop more servicable materials will require facilities for local preparation of ceramics with new binders. The acquisition of a hot press usage for sintering purposes is an important priority.

TECHNICAL PROGRESS FY 1980

Most Significant Results

Work on the program outlined above began on October 1, 1979. Since then the research has been primarily concerned with the structural characterization of hot pressed silicon carbide obtained from outside sources. TEM and electron diffraction analyses of "as hot pressed" SiC (+ 20% AlN) carried out by Dr. Zangvil on this project have indicated that a solid solution occurs only if the 2H SiC crystal structure is formed. Otherwise, a two-phase mixture of AlN and β -SiC (cubic) is formed with little apparent solid solution. The 2H SiC is seldom observed, in those cases where its presence has been observed there is reason to believe that some impurity (possibly aluminum) has stabilized structure. At least one of the cases cited above represents a non-equilibrium situation and it is not certain what role the impurities have on the crystal structure it has. - A systematic study on the effect that impurities have on the crystal structure must therefore be undertaken before research can proceed to a structural analysis of SiC grain boundaries where there is impurity segregation.

GAIN GROWTH IN ALUMINA

Principal Investigator: David S. Phillips
Assistant Professor of Metallurgical Engineering

ABSTRACT

The propensity of alumina for exaggerated grain growth poses problems to both the fabricability and service life of alumina materials. We are studying grain growth in both "pure" and doped alumina from both kinetic and structural perspective. Microstructural evaluation and particularly a search for grain-boundary segregants is in progress using the MRL analytical electron microscopy facility.

HYDROGEN TRAPPING IN BCC REFRACTORY ALLOYS

Principal Investigator: Theodore J. Rowland
Professor of Physical Metallurgy

Supporting Agency: U. S. Department of Energy

Senior Staff: Theodore J. Rowland, Professor

Junior Staff: Lih-Hsin Chou, Research Assistant
Peter E. Schleifer, Research Assistant

ABSTRACT

This project seeks to use the best techniques available to study the electronic and molecular structure of solids, and relate these to electrical and/or mechanical properties. In the past the work has focused at various times on metallic alloys, on polymers, and on organic semiconductors. Body centered cubic refractory metal alloys are of central interest in the current program, and will continue to be the main effort for some time into the future. The objective is to understand the major factors involved in the spatial distribution of hydrogen in bcc alloy systems. This information is relevant to the design of materials which are resistant to the hydrogen embrittlement problems that accompany hydrogen take-up in many structural bcc metals.

PURPOSE

In the broadest terms our purpose is to develop a reasonably complete understanding of the macroscopic behavior of hydrogen doped binary metallic solid solutions. An early goal is to characterize the change in local charge distribution and atom displacements which accompany the introduction of hydrogen into the alloy. The configuration will be determined by the characteristics of sites near solute and solvent atoms, and the consequent trapping of hydrogen in the material. This can inhibit the hydride formation believed to cause cracking in some cases.

Our research program will be to determine the hydrogen behavior in each of a selected group of binary single phase solid solutions. Some simple mechanical measurements will be made for reference purposes. The major investigation will then concentrate on the electrical and electronic modifications caused by the hydrogen.

We stress here that we are concerned with composition ranges for which hydride formation does not take place even as a minor second phase. Theoretical work complementing the studies briefly outlined above is being planned in cooperation with Argonne National Laboratory.

The fundamental aspects of this work are emphasized in our research program. However the results of the research have a direct applicability to practical metallurgical problems. The formation of hydrides is thought to be the first

step in several failure mechanisms involving hydrogen embrittlement. Alloys in which such hydride formation is diminished or eliminated can be expected to have improved resistance to failure.

TECHNICAL PROGRESS FY 1980

A scheme was developed for the reliable growth of large (roughly 2 cm x 2 cm x 0.4 cm) single crystals of the organic one-dimensional semiconductor methyltriphenylarsonium ditetracyanoquinodimethanide, $\text{Me}\phi_3\text{As}(\text{TCNQ})_2$. (Figure 1)

Fig. 1. As grown crystals of $\text{Me}\phi_3\text{As}(\text{TCNQ})_2$, about 2-4 mm thick. High conductivity and dielectric constant are parallel to a side shown here. We believe we have grown the largest and purest crystals of this compound in existence.

We observed a strong correlation between the size of the resulting crystals and the purity of the starting materials. Measurements of the electrical resistivity and dielectric constants were made as a function of crystal orientation. Markedly non-Ohmic behavior, Fig. 2(a), and a large, frequency

Fig. 2(a). Current i at voltage V , divided by i at one volt across the crystal. If the compound were Ohmic the broken straight line would be expected. The temperature independence of $i(V)/i(1)$ suggests tunneling as a source of this behavior.

and temperature dependent, dielectric constant were revealed in the direction of high conductivity. The latter is shown in Fig. 2(b). These phenomena were

Fig. 2(b). Logarithm of capacity (in high conductivity direction) vs inverse temperature for two different frequencies. The capacity (in fact the dielectric constant) continues to decrease with increasing frequency. The activation energy for the process is found to be 0.41 eV for both the dielectric constant (shown) and the electrical conductivity.

related to the impurity concentration, and the latter roughly determined both by electron paramagnetic and nuclear (proton) magnetic resonance. A physically plausible model in which impurities in the conducting chain act as potential barriers impeding the charge carriers was constructed. All facets of our observations were described by the model. In addition the model explained a slow change from non-Ohmic to Ohmic behavior with increasing temperature which has been noted by others working with similar materials. Several aspects of this work, will help to shed light on the electronic structure and the effects of doping in these materials.

PUBLICATIONS (Calendar Year 1979):

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Semiconductor Methyltriphenylarsonium Tetracyanoquinodimethane
Phys. Rev. Lett. 43, 879-992 (1979)

P. M. Lenahan and T. J. Rowland
Giant Dielectric Constant in the One-Dimensional Semiconductor $\text{Me}\phi_3\text{As}(\text{TCNQ})_2$
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NMR Relaxation Study of Crosslinked cis-1, 4-Polybutadiene
J. Polymer Sci. (in press)

STUDIES OF DISORDERED MATERIALS BY ELECTRON PARAMAGNETIC RESONANCE

Principal Investigator: Harvey J. Stapleton
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Supporting Agency: U. S. Department of Energy

Senior Staff: Harvey J. Stapleton, Professor

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ABSTRACT

Fast ionic conductors, amorphous semiconductors, and glasses are typical systems whose special properties depend upon a high degree of disorder. Electron spin relaxation, electron-nuclear double resonance (ENDOR), and electron spin resonance measurements on irradiation-induced paramagnetic centers in disordered materials are yielding data which characterize the additional low energy states unique to amorphous materials. Our relaxation data from a color center in the conduction plane of K, Li, and Na beta alumina exhibit anomalies in magnitude, temperature dependence, and microwave frequency dependence. We have developed a model for electron spin relaxation in glasses and successfully tested it using our data together with the low temperature heat capacity, thermal conductivity, and dielectric susceptibility data on beta alumina. Experiments still in progress include an ENDOR study of an F^+ center in beta alumina in order to map out the cation distribution in the conduction plane, and spin relaxation measurements on an F^+ center in lithium doped CaO because it involves relaxation by localized tunneling states having a very narrow energy distribution. Also planned are resonance experiments down to 0.25 K on amorphous silicon, produced by ion implantation, to determine its relaxation mechanism and the nature of the paramagnetic center common to amorphous silicon.

PURPOSE

Sensitive probes of disordered materials become available if one incorporates a paramagnetic defect within the structure. Frequently this can be accomplished by irradiation at low temperatures, but in the case of amorphous silicon, unpaired electron spins are intrinsic to the amorphous state. With such defects present, the powerful techniques of electron spin resonance, electron-nuclear double resonance (ENDOR), and electron spin relaxation become available to probe both the local environment surrounding the paramagnetic center and the system of states which interact with the spins and bring them to thermal equilibrium after some disturbance. In ordered materials the thermalizing system is usually the phonon bath, but in amorphous materials it is more likely to be the system of localized two-level tunneling states which have been so successful in describing the low temperature properties of glasses. Several important materials are currently under investigation using these three resonance techniques.

The structural disorder in sodium, potassium, and lithium beta alumina makes them fast ionic conductors with practical applications as solid electrolytes in batteries with high energy density. The disorder in the beta alumina is restricted to the sodium and oxygen containing planes which separate the Al_2O_3 spinel blocks. At low temperatures these materials behave as two dimensional glasses. Extensive data gathered in MRL by Professor A. C. Anderson describe the heat capacity, thermal conductivity, and dielectric susceptibility of beta alumina at low temperatures. These measurements have shown that beta alumina is a two dimensional glass that can be described by a system of localized two level tunneling states which interact strongly with the phonons and each other, and exhibit saturation effects characteristic of two-level systems. We have studied the EPR spectrum and spin relaxation rates of an F^+ center in K, Li, and Na beta alumina. These centers were produced by electron irradiation at low temperature using the MRL Van de Graaff accelerator. From the EPR spectrum we know that the center is in the disordered, conduction plane. The relaxation rate showed anomalies in magnitude, temperature dependence, and magnetic field dependence when compared to crystalline materials. In order to explain our relaxation data it was necessary to develop a model for electron spin relaxation via tunneling states in glasses. Published data on the parameters which describe the tunneling state system in beta alumina enable us to make a rigorous test of our model. ENDOR experiments on the F^+ center in the conduction plane of Na beta alumina have begun and preliminary data have been obtained. After analysis of these and similar data from K and Li beta alumina we expect to have detailed information about the mobile cations in the conduction plane of beta alumina.

One of the characteristic properties of tunneling systems in glasses is a density of states which is nearly constant up to some cutoff. The cause of this broad distribution of energies is not understood. It would be extremely useful to investigate systems in which the density of tunneling states could be varied so that the transition could be made from a real glass to one in which the tunneling states are isolated, non-interacting, and have sharply defined energies. For this reason we are investigating F^+ centers in lithium doped CaO , where the paramagnetic center is an electron trapped at an O^{2-} vacancy adjacent to a Li^+ which has substitutionally replaced a much larger Ca^{2+} ion. Such a system might be expected to possess sharp, non-interacting tunneling states. Our measurement of the F^+ relaxation rate is linear in temperature between 1.5 and 30 K, but the rate is 35 times faster in the lithium doped sample than in the undoped sample. Experiments with Na doping instead of Li are planned, as well as additional measurements down to 0.25 K which may show deviations from linearity that reflect the Li tunneling energies rather than the Zeeman energy of the F^+ center.

We are also reactivating the He-3 refrigerator system of our Ku-band microwave spectrometer in order to study amorphous silicon produced by ion implantation. Amorphous silicon yields an isotropic EPR signal with a g-value of 2.0055 and a linewidth of about 7 Oe at 10 K. We have measured the relaxation rate near 1.5 K and it is extremely rapid ($\sim 10^5 \text{ s}^{-1}$). By going as low as 0.25 K we expect to learn the mechanisms by which these electrons in amorphous silicon relax. In addition, since the isotropic EPR signal is probably motionally narrowed and the electron may freeze into shallow traps at 0.25 K, to produce

a broader, more structured EPR signal, this would yield microscopic information about the nature of the paramagnetic defect in amorphous silicon.

TECHNICAL PROGRESS FY 1980

Most Significant Results

We have discovered a new mechanism by which paramagnetic centers can relax in glassy materials. The glass is described, in the usual way, as being composed of a broad distribution of localized two level tunneling states which interact strongly with phonons. The electron spins relax via phonon induced transitions in which both a tunneling state of the glass system and an electron spin change their quantum states. This "forbidden" rate is much slower than the allowed one in which just a tunneling state makes a transition, and it is induced by a weak hyperfine coupling between the tunneling state and the spin. This coupling is due to the variation in the Fermi contact hyperfine interaction when a nucleus tunnels a distance d between the two wells of the glass tunneling state. This process is similar to proton relaxation in the presence of paramagnetic impurities but with two exceptions. The two level tunneling states, unlike paramagnetic spins, have a distribution of energy splittings and therefore a distribution of relaxation times. Secondly, protons near paramagnetic spins have shifted energy levels due to the strong dipole-dipole interaction, and this effectively generates a spin diffusion barrier which prevents the protons from rapidly achieving a common spin temperature during the relaxation process.

We have observed this mechanism as the dominant relaxation process for F^+ centers in the conduction plane of Na, K, and Li beta alumina. The paramagnetic centers are electrons trapped at O^{2-} vacancies at the O(5) site in the conduction plane of beta alumina. This disorder in the plane makes the beta alumina a two dimensional ionic conductor at high temperatures and a two dimensional glass at low temperatures. The F^+ centers exhibit anomalously large relaxation rates together with temperature and magnetic field dependences which are inconsistent with a normal spin-phonon interaction.

We had developed the basic elements of our relaxation model in FY 1979 using our data from Na beta alumina only, but several difficult details remained unsettled. As originally formulated, our model did not give the observed magnetic field dependence. Secondly S. K. Lyo and R. Orbach had independently proposed a slightly different relaxation mechanism which was independent of the magnetic field, but which predicted slower relaxation rates than either our model or the data indicated. We now solve the complete problem in a paper in which a correct blending of our model with that of Lyo and Orbach is carried through completely. The final result is that we can explain all the weak field dependence, the anomalous temperature dependence and the fast relaxation rates simultaneously. The fits to the data are shown in Figs. 1 and 2 below. Figure 1 shows the slight field dependence of the relaxation rate and the fit of our theory to the data. Figure 2 shows the variation of the relaxation rate with the mobile cation in beta alumina. Again the solid lines are fits with our model. In our fits of the relaxation rates, the contribution from the process suggested by Lyo and Orbach is less than 1% of the contribution from our process. In addition we fit the data to a power law in T and obtained exponents which are too high to agree with Lyo

and Orbach's approach, but are consistent with our model. We found it necessary to include phonon lifetime effects in glasses in order that our predicted magnetic field dependence be less than $1/H^2$. The localized tunneling state parameters for beta alumina, required to explain our relaxation data, remain in excellent agreement with previous heat capacity, thermal conductivity, and dielectric susceptibility measurements in that material.

Fig. 1. Electron spin relaxation rate of an F^+ color center in the conduction plane of Na beta alumina as measured at microwave frequencies of 9.5 and 16.5 GHz. The dashed and solid curves are the result of our model calculation.

Fig. 2. Electron spin relaxation rates of the F^+ color center in Na, Li, and K beta alumina. The curves through the data result from our model calculations.

Other Results: Because our work in the area of disordered materials is rapidly revealing important physical behavior, we have decided to move quickly into other areas associated with amorphous materials. We have therefore set aside our surface investigation, at least for the present time. In an effort to examine an even simpler tunneling system than beta alumina, we have made relaxation measurements on an F^+ center in lithium doped CaO. Here again the

paramagnetic center is an electron trapped at an O^{2-} vacancy, but now that vacancy is adjacent to a Li^+ ion which has substitutionally replaced a Ca^{2+} . We have measured the F^+ relaxation rate in CaO with and without Li doping. Between 1.5 and 30 K the electron spin relaxation rate in the doped sample is linear with temperature, independent of magnetic field, and about 35 times faster than in the undoped sample. The faster relaxation rate and lack of any magnetic field dependence suggest that the F^+ center is relaxing by the motion of the Li ion. If the Li is tunneling in the CaO lattice, its energy levels are probably sharp. This system would then be a useful starting point from which to make the transition to a true glass by increasing the Li concentration so that interactions between the tunneling states become important. Theories related to the broad distribution of tunneling state energies in glasses might then be tested. Further experiments with Na dopings are planned, since Na ions would be less apt to tunnel than the smaller Li ions. In addition we expect to further reduce our temperatures to 0.25 K using an existing He-3 refrigerator system. At these lower temperatures we may be able to determine if the critical energy in the relaxation is the Zeeman splitting of the F^+ center or some lower energy associated with the Li tunneling states.

We have also obtained some ENDOR data on Na beta alumina, but the spectrum is not yet understood. The Larmor frequencies of Na and Al are within 1.5% of each other and the experiment will have to be repeated using Li and K beta alumina. Using these ENDOR data we hope to map out the distribution of mobile cations around the F^+ center.

RELATIONSHIP TO OTHER PROJECTS

We are working closely with A. C. Anderson on these disordered materials. Most of our beta alumina samples were originally used in his low temperature measurements and we have made extensive use of that data in formulating our relaxation model for electron spins in glasses. Without that data it would not have been possible to make a rigorous test of our model. We also expect to collaborate with Anderson on our measurements of neutron irradiated MgO. The unirradiated MgO samples were provided for Anderson and us by M. M. Abraham of the Oak Ridge National Laboratory. Abraham is also working with us on the ENDOR study of the beta alumina and is providing us with the CaO samples containing F^+ centers and either Li or Na. Our theoretical work on electron spin relaxation in glasses is closely related to a theory (as yet unpublished) by R. Orbach (UCLA) and S. K. Lyo (Sandia Laboratories). Our current experiments on amorphous silicon are being performed in collaboration with Keith Brewer of Sandia Laboratory. He has provided us with amorphous silicon produced by Si ion implantation. He will be providing us with similar samples designed for optimum signals in our He-3 microwave spectrometer. It is necessary to cut the silicon samples first, then etch away the amorphous silicon due to the cuts, and then to reintroduce a layer of amorphous silicon by ion implantation.

The research of the principal investigator is also supported by a HEW grant (HEW PHS GM 24488) entitled "Electron Spin Relaxation at Active Sites in Proteins" with a current annual funding of \$34,400.

PUBLICATIONS (Calendar Year 1979):

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Electron-Spin Relaxation by Tunneling States in β - Al_2O_3 :Na

Phys. Rev. Lett. 42, 1883-1776 (1979)

S. R. Kurtz and H. J. Stapleton

Electron Spin Relaxation by Tunneling States in Na- β - Al_2O_3

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Fast Ion Transport in Solids: Electrodes and Electrolytes, P. Vashishta, J. N. Munday, and G. K. Shenoy, eds. (Elsevier North Holland, NY, 1979), pp. 319-322

S. R. Kurtz and H. J. Stapleton

Effects of Disorder on Electron Spin Relaxation in Beta Alumina, a Prototype Glass

Phys. Rev. B (submitted to)

KC-02-02-02 Experimental Research

LOW TEMPERATURE STUDIES OF DEFECTS IN SOLIDS

Principal Investigator: Ansel C. Anderson
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Supporting Agency: U. S. Department of Energy

Senior Staff: Ansel C. Anderson, Professor

Junior Staff: Eric J. Cotts, Research Assistant
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ABSTRACT

The purpose of this project is to obtain experimental data on a variety of defect structures, both to provide a basic understanding of the defects and to permit 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: thermal and electrical conductivity, specific heat, thermal expansion, ultrasonics and dielectric polarization. Current research includes the study of quantum-mechanical tunneling states in solid electrolytes and in radiation-damaged dielectric insulators, the transfer of thermal energy across interfaces, the dynamic behavior of dislocations, the interactions between defects, and general problems of heat transport in polymers, ceramics and composite materials appropriate to cryogenic engineering.

PURPOSE

The purpose of this project is to obtain experimental data on a variety of defect structures in solids, both (i) to provide a basic scientific understanding of the defects 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, and ultrasonic and dielectric dispersion. As one 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 various defect structures.

It is emphasized that materials and temperatures included in this investigation are inherent in any cryogenic scheme of energy production (e.g., fusion reactors,

superconducting generators), energy transport (e.g., superconducting transmission lines and peak-shaving magnets) or energy utilization (e.g., superconducting motors). As one explicit example of the applied importance of current research, we note that heat transfer along and across superconducting-insulator interfaces is a determining factor in the efficiency and thermal stability of the several superconducting devices mentioned above.

For the sake of clarity, six areas of research are discussed separately below. We do wish, however, to stress the cohesiveness of the research program. Progress in one area of investigation has been, and continues to be, closely related to parallel progress in other areas.

1. Disorder in Crystalline Solids. Ordinary glasses and plastics contain localized defects or excitations which dominate the low-temperature properties and which have a broad spectrum of frequencies or energies. These defects appear to be present in most amorphous materials. The defects are believed to be associated with some entity which tunnels quantum mechanically between two orientations having similar energies. We have shown that the crystalline superionic conductors $M\beta$ -alumina ($M = \text{Li, Na, K, Ag}$) contain these same defects in the disordered conducting planes, and hence that the defects can survive in a highly ordered environment. Previous work has not made clear why in a glass, but especially in β -alumina, the defects occur with such a broad range of frequencies. We have developed a theory which ascribes the broad frequency distribution to strain-induced interactions between the defects. This is somewhat analogous to "spin-glass" behavior in magnetic systems.

To study the interaction between defects we have undertaken two investigations. First, we are looking at the properties of single crystals containing impurities such as OH in KCl or CN in NaCl. The impurities can alter their orientation by a tunneling motion, and can interact with each other via both electric and elastic fields. Second, we have exposed single crystal quartz to neutron irradiation. The low-temperature properties are observed as the density of defects, and hence the interaction between defects, is increased with increased irradiation. Preliminary results are discussed below under Technical Progress.

2. Interfaces The impediment to heat flow through a nonmetallic material containing grain boundaries or between two different materials has been poorly understood. Theory and experiment have differed in the past by factors in excess of 10,000. In recent years we have demonstrated that a theory which correctly treats the reflection and refraction of thermal phonons at the interface can, with no adjustable parameters, correctly account for data obtained between 0.01 and 100 K for all types of materials, both crystalline and amorphous including commercial electrical insulators. There is one exception, namely the thermal impedance between an ordinary solid and a quantum liquid or solid (i.e., ^3He , ^4He , H_2 , D_2) at temperatures above ~ 1 K is not understood. This is a problem of practical importance since liquid ^4He is extensively used in cryogenic refrigeration. It has also been a frustrating theoretical problem in nonequilibrium processes. A new theory is published every few months. Yet the heat transfer process has

not been identified. There is some evidence that the process is associated with defects at the He-solid interface.

Two techniques have been used to measure the thermal resistance (Kapitza resistance) between solids and ^4He , but they give differing results. The "dc" technique is similar to the usual measurement of thermal conductivity; the "ac" technique utilizes the superfluid property of second-sound. We are using both techniques simultaneously on the same interface in an attempt to understand the cause of the different results obtained from the two methods, and perhaps thereby to better understand the heat-transfer process.

3. Thermal Expansion. It is difficult to obtain the volume dependence of the behavior of various defect systems since it is experimentally awkward to apply pressure to samples in a cryostat while measuring, for example, the thermal conductivity or specific heat. Hence, to provide some of this information, we are attempting to develop a thermal-expansion apparatus sensitive to the extremely small changes in volume or length which occur near or below 1 K. Since standard techniques are too insensitive, we are using a Josephson-effect, superconducting dilatometer (see below under Technical Progress). If the device is reliable, it will be applied to a study of several defect systems including the "tunneling" defects in disordered materials, the tunneling defects associated with H or D in Nb and other metals, and dislocations.

4. Specific Heat of Copper. During an earlier study of the tunneling of H and D in V, Nb and Ta, we measured the specific heat of pure copper as a test of a calorimeter. We observed an anomalous contribution to the specific heat at low temperatures. The measurement has been repeated on a sample from a different vendor, and the same anomaly is observed. The data agrees with other measurements from Bell Labs and at Berkeley. Such anomalies indicate the presence of excitations or defects; generally such defects are associated with impurities which may be magnetic in character. However our samples appear not to contain sufficient impurities to account for the anomaly.

We wish to pursue the question of the anomaly to determine if the analytical techniques used to measure trace concentrations of impurities are not as quantitative as believed, or if possibly (and less likely) the anomaly and the related excitation is intrinsic to pure copper.

5. Dislocations. The presence of dislocations in most crystalline materials greatly reduces the phonon thermal conductivity. We had shown previously that the strong phonon scattering occurs because the phonons undergo a resonant or dynamic interaction with the dislocations. Those measurements were obtained on crystals having rather small dislocation densities ($\approx 10^7 \text{ cm}^{-2}$). We have some evidence that the resonant interaction is suppressed at large dislocation densities. We therefore plan to extend our measurements to the high density regime. Other laboratories have already made measurements that do not extend over a sufficiently broad temperature range or to sufficiently low temperatures, to fully identify a possible resonant character of the phonon-dislocation interaction.

In addition to thermal transport measurements, we will also measure the specific heat of the deformed crystals. If the dislocations contribute significantly to the specific heat, as claimed by some authors, the data will provide both an independent determination of the spectral density of dislocation resonances, plus information concerning the physical nature of the resonant motion of the dislocation.

Initial measurements will be on LiF, since the behavior of dislocations at low densities is best understood in this material.

6. Cryogenic Materials. We plan to continue measuring various properties of new commercial materials as they become available and if they appear attractive for some cryogenic application. In the recent past, we have studied specialized plastics, ceramics, and glassy carbons.

TECHNICAL PROGRESS FY 1980

Most Significant Results

1) Interaction between dipolar defects in dielectric crystals. In this investigation (see Sec. 1 under PURPOSE) the measurement technique has been dielectric dispersion, since both temperature and frequency are readily varied, and samples of small size easily prepared. The results are unusually rich in information. A plot of dielectric absorption is shown in Fig. 1 for KCl containing ~ 1500 ppm OH^- and measured at 4000 Hz. Peaks 1 and 2 have activation energies of roughly 50 K and 200 K. From observations of the dependences on temperature, frequency, concentration, and isotopic (OH/OD) mass, the peaks 1 and 2 appear to be caused by electric-dipole, impurity-impurity interactions at nearest neighbor distances. The activation energies are consistent with such an interpretation. Insufficient data have been obtained on peaks 3 and 4 to attempt an identification.

We have not observed the slight "cusp" in the dielectric constant which recent theory says should be present if the population of electric dipoles (OH^-) undergoes a spin-glass-like transition. Indeed, our observation of apparent

discrete interaction energies for different near-neighbor positions is very similar to data obtained on the magnetic material $(\text{Eu}_x\text{Sr}_{1-x})\text{S}$ at Julich. In this material discrete interaction energies are observed only below the percolation limit of $x \approx 0.13$, i.e., at concentrations for which no spin-glass behavior occurs. Thus, by analogy, the failure to observe an electric spin-glass transition in $\text{KCl}:\text{OH}$ may be a result of a small concentration of OH^- . If true, the limited solubility of OH^- in KCl precludes the possibility of spin-glass behavior in this material. In this case, we will move on to other dielectric systems.

2) Radiation induced defects in crystalline quartz. Neutron irradiation produces a complex spectrum of low energy excitations in crystalline quartz. A portion of this spectrum is revealed in Fig. 2, which is a plot of

heat capacity divided by the cube of the temperature. In such a plot, the measured phonon contribution prior to irradiation is shown by curve 1. Irradiation at $\approx 10^{19}$ neutrons/cm² produces curve 2. (The excitations introduced by the γ -ray component in the reactor environment are removed by a 390°C thermal bleach.) There is in curve 2 both a Schottky peak at 1 K and a lower temperature, $C \propto T$ contribution appearing below ≈ 0.5 K. The Schottky peak can be removed by thermally bleaching at $>800^\circ\text{C}$ as indicated by curve 3; this treatment does not change the $C \propto T$ term.

The origin of the Schottky term is not known as yet. It apparently has not been reported previously in the literature. The $C \propto T$ is caused by localized excitations like those found in amorphous materials. This identification is supported by our thermal conductivity measurements and by ultrasonic measurements made elsewhere. Our work shows that the localized excitations appear even at neutron doses as small as $\approx 10^{17}$ cm⁻², in which case there is relatively little damage in the crystal. This is further proof that the localized excitations, believed to be due to quantum mechanical tunneling of atomic sized entities, do occur in highly crystalline environments as well as in amorphous materials. This result casts doubt on the theory, mentioned in Sec. 1 under PURPOSE, which relates the broad energy spectrum of the excitations to the elastic interaction between excitations. The present defect density would appear to be too small for this theory to apply.

Other Results

1) Specific Heat of Copper. We have shown that the anomalous low temperature specific heat of copper (see Sec. 4 under PURPOSE) does reproduce in high purity materials obtained from different vendors and with different histories of preparation. If the anomaly is caused by an impurity, this impurity is indeed ubiquitous.

2) Technical Developments. i) Thermal expansion (see Sec. 3 under PURPOSE). At an early state of development, the dilatometer has a resolution of $<5 \times 10^{-3}$ Å. It uses SQUID as a detector of displacement, the SQUID output is returned to a transducer to null the detected displacement and hence improve linearity and stability. A low-frequency, square-wave temperature variation is applied to the sample. The signal-averaged output thus gives thermal expansion directly.

ii) Germanium thermometry. For the past six years we have worked on the development of Ge resistance thermometers for very low temperatures, on the development of instrumentation for those thermometers, and towards the realization and maintenance of the T₇₆ temperature scale. The work has been done in cooperation with the National Bureau of Standards, Cryo-Cal Corporation and Lake Shore Cryotronics. We have demonstrated what precautions are necessary to provide 1% or better accuracy at temperatures down to 30 mK.

iii) We have started the installation in an rf-shielded room of a new ³He-⁴He dilution refrigerator which will eventually replace our 12 year old machine. The new refrigerator will have a lower ultimate temperature, greater refrigeration capacity, and a more simple and reliable provision for SQUID technology. This refrigerator was cost-shared between DOE, NSF and University of Illinois funds.

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 amorphous materials is carried out under NSF Grant DMR-77-08599. It includes work on glasses, polymers (including rubber), and glassy metals, and the effects of radiation damage, thermal history, etc. on those materials. We have obtained considerable information concerning the localized excitations associated with disorder. This research is mentioned here because a) some facilities developed under the present contract have been used, and b) the results of the NSF project have been very important in analyzing the results of work supported by DOE. For example, we have been able to explain the thermal conductivity behavior of partly crystallized ceramics, porous materials, and the recently developed glassy carbons.

Within this laboratory we have developed an excellent facility for obtaining a variety of measurements in a temperature range four decades wide, 0.02 - 300 K. Because of the broad spectrum of materials investigated, it is not feasible to prepare all the 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 have collaborated with H. K. Birnbaum, (Metallurgy) on H or D in Nb, V and Ta; with T. J. Rowland (Metallurgy) and D. S. Pearson (previously of Northwestern University) on polybutadiene; and with C. B. Satterthwaite (Physics) on H or D in Pd. There has also been collaboration with laboratories at Corning Glass Works on glasses; Allied Chemical and Bell on glassy metals; MMM 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.

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RESPONSE OF SOLIDS TO ELECTROMAGNETIC RADIATION

Principal Investigator: John D. Dow
Professor of Physics

Supporting Agency: U. S. Department of Energy

Senior Staff: John D. Dow, Professor
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ABSTRACT

The theory of electronic excitations in disordered structures is being used to treat deep defect levels in amorphous Si and modified amorphous Si, in an attempt to better understand how these impurity levels limit the performance of photovoltaic devices.

The theory of the electronic shock wave created when synchrotron radiation excites metals is being developed for comparison with x-ray absorption, emission, and photoemission experiments and with Auger electron emission.

The effects of surface relaxation, adsorbates, and intercalates on low energy electron diffraction spectra and photoemission angular distributions of transition metal dichalcogenides are being studied using a new multiple scattering theory.

The theory of electronic excitations in three-dimensional alloys is being developed using an embedded cluster technique which successfully describes the vibrational spectra of one-dimensional binary and ternary alloys.

PURPOSE

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) the theory of electronic excitations in crystalline and amorphous alloys and amorphous Si, in particular; (ii) studies of the role of electronic relaxation in determining the synchrotron radiation spectra of metals; (iii) attempts to understand the low energy electron diffraction (LEED) spectra of transition metal dichalcogenides, and (iv) studies of the effects of rare gas and alkali adsorbates and of alkali intercalates on LEED and photoemission angular distribution spectra of transition metal dichalcogenides.

The theory of a-Si is meant to predict the impurities or combinations of impurities which, when added to pure a-Si, are likely to reduce the non-radiative carrier lifetimes and to improve a-Si as a potential efficient solar-cell material.

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.

Studies of LEED and photoemission angular distribution spectra of transition metal dichalcogenides have concentrated on developing the theoretical tools necessary for determining relaxation of the surface layers of these materials. With these tools in hand, we are now embarking on structural calculations for surfaces perturbed by adsorbates and intercalates.

There are a number of practical aspects of our work highly relevant to DOE's energy mission. Amorphous Si (a-Si) is a strong candidate for a practical solar cell because it can be inexpensively deposited and promises to have a reasonable efficiency. To produce a device efficiency great enough to applications, a-Si will most probably need heavy doping with a modifier impurity. The role played by modifiers in improving the efficiency is poorly understood at present. We propose to execute theoretical calculations to better understand the basic physics of modifiers in a-Si.

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.

TECHNICAL PROGRESS FY 1980

Most Significant Results

A theory of core excitons in semiconductors has been developed, and a new kind of Frenkel exciton has been predicted. The nature of the Wannier to Frenkel exciton transition has been elucidated and the first predictions of the major chemical trends in exciton energies have been made. The theoretical machinery developed for this work will provide the foundation for our future work on modifiers in amorphous Si.

The excitation of metals by synchrotron radiation causes an electronic shock wave to propagate out from the x-ray created core holes. Previously only an asymptotic theory of this effect had been given: the shock-wave effect manifests itself as a characteristic synchrotron radiation absorption or emission lineshape. In collaboration with C. P. Flynn, C. A. Swarts, and M. A. Bowen, we have developed a theory of this effect, which predicts significantly different lineshapes from those of the previous approximate theory. The roles of s- and p-waves have been determined; and the work is now being extended to Auger spectra. It is already clear that major revisions of our present understanding of electronic relaxation in metals will follow. With the techniques we have developed, it is possible for the first time to compute the effects of electronic relaxation on the excitation spectra of metals and alloys.

RELATIONSHIP TO OTHER PROJECTS

This theoretical project cooperates with and assists various experimental programs at the University of Illinois. 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 ONR and JSEP on deep traps in semiconductors and molecular beam epitaxy of semiconductors.

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 non-free electron like. At the present we are engaged in collaborative research with groups at Northwestern, Cal-Tech, Texas Tech, Western Illinois, SERI, and Texas A and M.

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Ph.D. thesis, Physics, J. D. Dow, adviser (1979)

(Also supported by ONR)

Donald Lynn Miller

Studies in the Electronic Structure of Matter

Ph.D. thesis, Physics, J. D. Dow, adviser (1979)

(Also supported by ONR and NSF)

Coenraad Albert Swarts

Studies in the Electronic Structure of Matter

Ph.D. thesis, Physics, J. D. Dow, adviser (1979)

(Also supported by NSF and ONR)

USE OF VERY HIGH PRESSURE TO INVESTIGATE THE STRUCTURE OF MATTER

Principal Investigator: Harry G. Drickamer
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ABSTRACT

The central theme of our research is the use of very high pressure to understand the electronic properties of materials. Ultimately, new or improved materials can be designed from the basis of this understanding.

The basic effect of pressure is to decrease interatomic distance and to increase overlap between adjacent electronic orbitals. Techniques have been developed which permit optical absorption and luminescence, electrical resistance, Mössbauer resonance, and x-ray diffraction measurements to several hundred kilobars. Application of these techniques to a wide variety of systems has added to the understanding of the electronic states and of electronic transitions to new ground states with different physical and chemical properties have been observed. At present, the emphasis is on the study of luminescent photoconducting and photochemical properties of both organic and inorganic systems, and the testing of theories concerning phosphor efficiency and lifetime, energy transfer, and the mechanism of photochemical reactions.

The ultimate goal is to contribute to more efficient production of light and of conversion of light to chemical, thermal or electrical energy.

PURPOSE

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 nanosecond.

We plan to expand our research program in two directions: (a) intensification of our studies of glasses, polymers and very viscous liquids and (b) photoionization and photoconductivity on organic solutions. In this way we will extend our research efforts both to new materials and to new measurements in high pressure science.

TECHNICAL PROGRESS FY 1980

Most Significant Results

(1) Emission characteristics of $\text{La}_2\text{O}_2\text{SiEu}$ and $\text{Y}_2\text{O}_2\text{:Eu}$. These phosphors are important in a number of applications including fluorescent lights, screens, and as phototypes for rare earth lasers. The question to be answered is as follows. The excitation takes place via ligand to metal charge transfer with an energy of 4.2 - 4.3 eV. This excited state is supposed to go over

immediately to excited Eu^{+3} levels $^5\text{D}_0$, $^5\text{D}_1$, $^5\text{D}_2$, and $^5\text{D}_3$ (split by spin orbit coupling). These lie in the range 1.9 - 2.9 eV, so all should be fed from the CT state. Yet at one atmosphere emission is observed only from $^5\text{D}_0$ and $^5\text{D}_1$, with an additional trace from $^5\text{D}_2$ at very low temperature. Struck and Fonger have proposed a configuration coordinate diagram as is shown in Fig. 1, but it has not hitherto been thoroughly verified. The CT

Fig. 1 Configuration coordinate diagram for $\text{La}_2\text{O}_2\text{SiEu}$ as proposed by Struck and Fonger. The dotted line represents the observed location of the charge transfer peak at 100 kilobars.

state does indeed feed into all the ^5D states, but their intrinsic lifetimes are of the order of hundreds of microseconds, and for $^5\text{D}_3$ and $^5\text{D}_2$ the barrier for back-feeding into the CT state is so low that all excitations are degraded from these levels via the CT state to $^5\text{D}_1$ and $^5\text{D}_0$. If the diagram correctly locates the CT state along the totally symmetric coordinate, pressure should increase the energy of the CT state vis á vis the ^5D levels (as shown by the dashed curve) decreasing the probability to back-feeding. Thus, with pressure, the radiation from $^5\text{D}_0$ and $^5\text{D}_1$ should decrease because less excitation gets to them, $^5\text{D}_2$

and ultimately $^5\text{D}_3$ should appear. The CT state does shift to higher energy by $\sim 0.25 - 0.3$ eV in 120 kilobars. The effect on the emission intensities is summarized in Fig. 2. We see the expected decrease in $^5\text{D}_0$ and $^5\text{D}_1$ intensity, a large increase in $^5\text{D}_2$ emission which finally levels and drops beyond 80-90 kilobars, while $^5\text{D}_3$ appears at ~ 70 kilobars and increases rapidly in intensity. The various peak intensities balance out to give constant total intensity with pressure within our ability to determine it. From the barriers to back-feeding at one atmosphere given by Struck and Fonger, and the shift of the CT peak with pressure one can approximate the decrease in backfeeding probability and consequent increase in $^5\text{D}_2$ and $^5\text{D}_3$ emission intensity. This is shown in Fig. 3. The argument is quite satisfactory for so simple a classical calculation.

The lifetimes are also consistent with the analysis. For $^5\text{D}_0$ and $^5\text{D}_1$ they are independent of pressure, since one is only varying the feeding rate. For $^5\text{D}_2$ the lifetime increases with pressure to 40 kilobars and is then constant, while for $^5\text{D}_3$ the lifetime increases rapidly with pressure. The results for $\text{Y}_2\text{O}_2\text{S:Eu}$ are quantitatively quite different but are also entirely constant with the analysis.

These results demonstrate the power of pressure to give a definitive test of an analysis for a technologically important material.

Fig. 2 Intensity changes with pressure for the emission from the 5D_0 , 5D_1 , 5D_2 and 5D_3 peaks of Eu^{3+} in $\text{La}_2\text{O}_2\text{S}:0.1\%\text{Eu}$.

Fig. 3 Measured intensity changes for the emission peaks with pressure compared with the changes predicted from the shift of the charge transfer peak (5D_2 and 5D_3 emission in $\text{La}_2\text{O}_2\text{S}:\text{Eu}$).

(2) Excimer emission and conformation and motion in solid polymers using polyvinylcarbazole as a probe.

The emission of polyvinylcarbazole (PVCA) has been widely studied because of its practical applications. At one atmosphere in solution or in the solid polymer there exists two peaks one at ~ 430 nm and one at ~ 380 nm. These are both caused by emission from excimer (excited state dimer) states but involve different rate controlling steps. We have studied the effect of pressure on emission intensities of these two peaks in PVCA film and with PVCA as a dilute solute in polymethylmethacrylate (PMMA), polystyrene (PS) and polyisobutylene (PIB). In all cases the low energy peak grows strongly in intensity at the expense of the high energy peak with increasing pressure. A plot of relative intensity of the two emissions vs pressure (Fig. 4) shows two regions; at low pressure a relatively steep line and a high

pressure line of shallower slope. (In Fig. 4 we show only the low pressure region. The data extended out to 40 kilobars without further change of slope).

The break in the slope occurs at 2 kilobars for pure PVCA, at 4 kilobars for PVCA in PS, at 6 kilobars for PMMA and at 14 kilobars for PIB. Clearly there are two mechanisms one dominant at low pressure and one at high pressure.

A rather extensive analysis presented in the paper indicates that in the low pressure region it is possible to rearrange the type one site into a type two site by a rotation with a consequent change in volume ΔV_{12} shown in Table I. In the high pressure region one is affecting only the equilibrium constant for an excitation to be trapped by a type one or type two site. No change in the number of available type two sites is possible. One can extract from these pressure data the change in volume of the system ΔV_c when a type two site is excited instead of a type one. There are also listed in Table I, as are the glass transition temperatures from the four solvent

Fig. 4 Relative intensities of the low energy to the high energy emission peaks for excimer emission of polyvinylcarbazole in various media. The steep slope at low pressure represents the dominance of the process of formation of excimer sites by rotation. The smaller slope at high pressure shows the difference in volume between the two excimer sites.

Table I

ΔV 's and T_g 's of PVCA in All Host Polymers

Polymer	(high pressure) ΔV_c (cm ³ /mole)	$\Delta V_c/V_{mol}$	(low pressure) ΔV_{12} (cm ³ /mole)	$\Delta V_{12}/V_{mol}$	T_g °K
PVCA film	-2.0	0.011	-5.1	0.028	480
PVCA in PS	-1.6	0.009	-5.0	0.027	375
PVCA in PMMA	-1.1	0.006	-3.9	0.021	325
PVCA in PIB	-0.9	0.005	-2.1	0.012	200

polymers. Both the location of the pressure where motion ceases and the volume change associated with the low pressure motion correlate very well with T_g . It is clear that some significant rotation is possible below T_g but it requires a bigger volume change in the more rigid media and is frozen out at lower pressure. These are more detailed results than have hitherto been obtained concerning localized motions of solid polymers as a function of pressure, and are particularly interesting for PVCA which is useful in photoreproduction processes.

(3) Fluorescence of Polyenes

The diphenyl polyenes are widely studied compounds important as prototypes for molecules important in photoreproduction processes and for the behavior of molecules essential to vision. Analyses have indicated that the radiative rate k_f should be proportional to $(\Delta E)^{-2}$ where ΔE is the energy difference between the lowest vibrational level of the emitting state and a weighted average of the vibrational levels for the absorption spectrum. This last quantity can be approximated by ΔE_{0-0} except at quite low values of ΔE . Efforts to test this analysis by the use of various solvents have proven equivocal. We have studied diphenyl hexatriene (DPH) and diphenyl octatetraene (DPO) using pressure as well as various solvents. Fig. 5 shows some of the results. They indeed confirm the theory for values of ΔE greater than about 1000 cm^{-1} . A similar test was applied successfully to these molecules in polymeric solvents to 40 kilobars pressure.

Fig. 5 Correlation of the radiative rate with Stokes shift, providing a test of the predictions $k_f \propto (\Delta E)^{-2}$, for two polyenes in various media

Other Results

Fluorescence depolarization studies

In last year's report we mentioned the development of an apparatus for measuring fluorescence depolarization at high pressure. In particular, the method can be applied to studying relaxation effects for polymers in solution. Our studies on polyacrylamide indicate a small molecular weight dependence of the depolarization which indicate that the motional process involves the cooperative action of only a few (~ 10) monomeric units.

In cooperation with Professor G. Weber of Biochemistry we have obtained useful information concerning relaxation and changes of conformation of the proteins lysozyme and chymotrypsinogen through similar studies of fluorescence depolarization.

New Techniques

In connection with our studies of the effects of very high viscosity on luminescent phenomena we have developed a high pressure viscometer capable, we believe, of measuring viscosities to at least 10^4 poise. It is now operable but only a few data have been obtained mostly in the form of calibration of fluids of known viscosity.

An important extension of our work involves the use of time resolved spectroscopy to separate emissions on different time scales and to see the change in emission spectra with time e.g., in a very viscous media. The electronics for these studies has been developed and is operable. For many of the studies of interest a more intense pulsed light source is necessary. A nitrogen triggered dye laser has just been delivered, and when it is put into operation we shall be able to proceed with time resolved spectra.

RELATIONSHIP TO OTHER PROJECTS

Work to be initiated in the next year on luminescent probes in glasses could have a significant impact on uses of glass for various optical and catalytic purposes.

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.

The Principal Investigator has no contract support from sources other than the Department of Energy.

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Larry Alden Brey

High Pressure Photophysics of Organic Molecules

Ph.D. thesis, Chemical Engineering, H. G. Drickamer, adviser (1979)

George S. Chryssomallis

High Pressure Polarized and Unpolarized Fluorescence Studies
of Macromolecules

Ph.D. thesis, Chemical Engineering, H. G. Drickamer, adviser (1979)

Martin I. Finston

Photoconductivity Studies of the Ferrocyanide Ion Under High Pressures

Ph.D. thesis, Physics, H. G. Drickamer, adviser (1979)

Michele M. Thomas

High Pressure Studies of the Toluene-s-Tetracyanobenzene Complex

M.S. thesis, Chemical Engineering, H. G. Drickamer, adviser (1979)

Grant A. Webster

The Effects of High Pressure on the Luminescence of Europium Doped
Lanthanum and Yttrium Oxysulfides

Ph.D. thesis, Chemistry, H. G. Drickamer, adviser (1979)

EXCITON COLLECTION FROM ANTENNA SYSTEMS INTO ACCESSIBLE TRAPS

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ABSTRACT

Interfacial photochemistry can be driven by light absorbed elsewhere and transmitted by exciton propagation to the interfacial region. This project concerns the conditions for propagation and collection of energy at interfaces in thin film systems. The materials of concern are molecular solids, including crystalline aromatic species and dispersions of aromatics in polymers, such as polystyrene. Exciton traps are typically submonolayer surface coverages of a polycyclic hydrocarbon on a thicker film (1000-5000Å) containing the antenna chromophore. Propagation and collection of excitons is being explored by steady-state and time-resolved fluorescence spectroscopy. Other work involves the development of methods for creating thin film assemblies of molecular materials via vacuum processing techniques and methods for the microstructural characterization of such systems.

PURPOSE

Our research group is interested in thin films (less than one monolayer to 10,000 Å in thickness) in assemblies (several films overlaying one another), because they allow one to create environments where chemical processes can occur under special conditions. In general, we want to study electron transfer processes taking place in the asymmetric environments at film interfaces. We are particularly interested in light-driven electron transfers, hence we are also concerned with certain photophysical processes leading up to the chemical event.

One ultimate target is a general means for preventing recombination after light-induced electron transfer from a donor molecule D to an acceptor species A, e.g.,

The charge separated state A^+D^- represents a high energy chemical embodiment of the absorbed photon. If it could be utilized at leisure, it could be a

very fruitful vehicle for the conversion of light energy, including solar energy. The problem is the recombination step, which thermalizes the energy. This process is always exothermic and always presents a threat to such a scheme. Interfaces in thin film assemblies offer some promising possibilities for blocking the process, because they possess the inherent asymmetry needed to enforce carrier separation at the AD reaction center.

A limitation of placing photochemical reaction centers at an interface is that only a small amount of light can be absorbed at the centers themselves.

For efficient utilization of the light, one needs an antenna system of chromophores which can collect the light over a large, three dimensional domain and transmit its energy as excitons to the reaction centers, where the apparatus for carrier separation can be localized. It is significant that photosynthetic organisms employ just this strategy to maintain a simplicity of design. We have been able to mimic the effect in assemblies of thin films, and this aspect of our work is the major point of this proposal.

We are also concerned with methods for making devices from molecular materials and a component of our work involves research into the fabrication and characterization of appropriate film assemblies.

TECHNICAL PROGRESS FY 1980

Most Significant Results

Our work has concentrated on a system (Fig. 1(a)) in which the photoreceptor fluoranthene is dispersed in to a polystyrene matrix with 15-30 Å mean spacing between chromophores. The fluoranthene/polystyrene phase is cast into a film of 1000-4000 Å thickness on a glass substrate. Perylene is placed as an exciton trap on the outer surface of the polystyrene at sub-monolayer coverage. The amounts of the substances involved are precisely determined via bulk fluorometric analysis of solutions made by dissolving the film assemblies. Irradiation of this kind of assembly leads to strong luminescence from the perylene surface sites, which become excited by trapping energy that is initially absorbed in the fluoranthene/polystyrene phase.

Evidence for such an antenna effect includes the following points: (a) Placement of the perylene causes a transformation of the emission spectrum of the system from that of dispersed fluoranthene to a mixed distribution with a predominant perylene component. This is true even though perylene contributes less than 1% of the absorbance at the usual excitation wavelength. (b) The excitation spectrum of the perylene component is identical to the excitation spectrum of fluoranthene. (c) Placement of the perylene quenches the fluoranthene emission by 10-30%.

These points show that the trapping center is indeed being fed by energy absorbed initially by fluoranthene. The degree of quenching suggests that the range of exciton collection could be as high as 500 Å.

The perylene can be demonstrated to be a surface trap by adding a 20 Å overlay of gold. (Figs. 1(b) and (c)). The overlay selectively quenches the perylene emission entirely, and there is no regrowth of the component over a several-day period.

The most straightforward explanation for our observations is to propose that excitons migrate among fluoranthene sites until they approach the surface sufficiently closely to be trapped, probably by Förster's transfer, in a perylene site. Since the singlet of perylene lies about 0.3 eV below that of fluoranthene, the trapping effect should be essentially irreversible.

The molecular requirements for an effective antenna system make up a topic of extensive current research. Emphasis is being placed on photosynthetic systems and on models of photosynthetic apparatus; and the points of major concern are the required concentrations of chromophores and the conditions of relative alignment. The exciton collection distance indicated by our work is surprisingly large for a system of dispersed, randomly-oriented chromophores. Its magnitude suggests that effective antenna regions might be synthesized without special alignments among chromophores and without very high chromophore concentrations.

The contribution of thin film techniques to this problem is in the production of accessible trapping centers. One is left with considerable freedom to assemble additional apparatus to ensure that the trapped energy is actually used effectively.

Two major outstanding questions concern the uniformity of the fluoranthene distribution within the polystyrene phase and the mechanism by which energy is coupled to surface traps. Progress regarding both has been made in the past year.

During that period, we have completed an apparatus for measurement of fluorescence transients by the time-correlated single photon counting method. The heart of the system is a set of purchased modules from EG&G Ortec, but we have added a custom-built interface to allow our laboratory computer to assume the functions of a multichannel analyzer. Software for collection and analysis of data is complete. For about the past six months, we have been using the system on a routine basis to study luminescence transients from film assemblies.

A good deal of the work has involved films with tetrabromo-o-benzoquinone (TBBQ) cast homogeneously into the fluoranthene/polystyrene matrix. The TBBQ molecules are singlet quenchers, and their effect on luminescence from fluoranthene will provide information about the effectiveness of exciton movement among fluoranthene sites. These experiments were designed to clarify this important aspect without complicating the problem with the special geometric features of surface traps. Existing theory can be used to interpret the results. Fluorescence decay curves have been recorded for systems with fluoranthene and TBBQ concentrations both varying over two orders of magnitude. Parallel quenching curves from steady-state fluorescence measurements have also been compiled. Now in progress is an analysis of these results that will permit an evaluation of the diffusion coefficients of fluoranthene excitons. We expect to offer a publication based on this work within two months.

A good deal of effort has been spent on structural aspects of the two-layer assemblies of Figure 1(a). We are particularly concerned about the possi-

bility that a surface excess of fluoranthene exists near the outer boundary of the film. The estimated range of collection cited above rests essentially on an assumption that excitons are initially created uniformly throughout the polystyrene/fluoranthene phase. The existence of a surface excess of fluoranthene within a short distance (e.g., a Förster radius) of the surface would compromise that idea and change the interpretation significantly.

Extensive measurements have been made with 20 Å (nominal) gold layers as quenching films in contact with the fluoranthene/polystyrene phase. The gold mirror interacts with fluoranthene singlets over rather large distances ($\sim 300 \text{ \AA}$) and quenches its luminescence; thus the degree of quenching serves as an index of the fluoranthene population within 300 Å of the surface. Two separate configurations were compared: (a) Fluoranthene/polystyrene over gold over glass and (b) Gold over fluoranthene/polystyrene over glass. The mean degree of quenching was essentially the same in sets of replicates for configurations (a) and (b), thus the lower and upper interfaces seem to be equivalent. If an excess exists at the top, it also is present at the bottom. However, these results and other dealing with the degree of quenching by gold vs. film thickness and fluoranthene concentration tend to suggest that there is no surface excess. This work is included in a comprehensive paper on the two-layer systems, which has just been submitted for publication.

A direct attack on the problem of fluoranthene distribution was carried out via the thin film analytical tools available in our Materials Research Laboratory. However, other organic solutes had to be substituted for fluoranthene, because one cannot distinguish readily between fluoranthene and

polystyrene by Auger, SIMS, or ESCA measurements. We chose to examine dispersions of hexabromocyclododecane and octafluoronaphthalene in polystyrene, in hopes that the halogens could be observed in Auger depth profiles. Useful results were not obtained, because the halogens proved uniformly invisible. We believe that the electron probe may have caused local heating of the matrix above the glass transition of polystyrene, so that the small molecules were lost by diffusion and volatilization into the surrounding vacuum. Additional efforts with lower beam currents are planned.

We have also examined certain ageing phenomena in the two-layer systems of Figure 1(a). In general, we find that the efficiency of energy coupling improves for about 10 hr after assembly, then further improvement ceases. This result may reflect penetration of perylene molecules into the polystyrene phase for a distance of a few tens of angstroms or it may reflect aggregation of perylene on the surface. We are hoping that careful study of the perylene emission spectra will give useful clues about possible environmental changes.

A collaborative effort with Dr. David Whitten of the University of North Carolina (Chapel Hill) has begun to yield results. Dr. Whitten is a practitioner of monolayer deposition by the Langmuir-Blodgett method, and we hope to use that technique to place immobile surface traps on fluoranthene/polystyrene phases with better architectural control than we now have. Initial work is proceeding with a surfactant version of tris(2,2'-bipyridyl)ruthenium(II), which has very interesting photophysical and photochemical properties. Monolayer deposits on polystyrene have been excellent in trials, and the first group of fluoranthene/polystyrene-coated plates is now being treated with the surfactants in Whitten's laboratory.

Our work requires better tools for the chemical characterization of thin-film assemblies than we now have available. Problems cited above with respect to Auger profiles are typical: Chemical specificity is lacking and beam damage in molecular solids is uninvestigated. We are attempting to develop procedures for dealing with these kinds of systems on Auger, SIMS, and ESCA equipment, in collaboration with Dr. Peter Williams of the Materials Research Laboratory. Some very useful results have been obtained on two-layer phthalocyanine systems. A typical case involves a glass substrate coated with 10,000 Å of silver, then 2000 Å of magnesium phthalocyanine, and finally 2000 Å of manganese phthalocyanine. The object is to ascertain the sharpness of the interface between the two phthalocyanines by monitoring the metals in them, and to find the extent to which interdiffusion is promoted by thermal processes upon storage and by beam damage during profiling. We have found that an interface region perhaps 200 Å thick exists indefinitely in samples stored at room temperature or below. This dimension, typical of grain sizes in the materials, indicates that interfacial characterization can be carried out without severe beam-induced mixing. Thermal interdiffusion is observed at temperatures above 150°. A paper describing these results and other studies in progress will be presented at the spring meeting of the Electrochemical Society. A written report should be submitted for publication at about the same time.

Other Results

Support from this grant has also gone, at a fairly low level, into the completion of a high-performance fluorescence spectrometer in our laboratory. This general facility possesses double monochromators in both optical beams in order to handle samples that tend to scatter the excitation light. That problem is a constant difficulty in our studies of steady-state luminescence from films. The spectrometer also offers an excitation-beam flux monitor and computer-controlled data acquisition and spectral correction. These features are extremely useful for work with films. Two recent reports, listed above, describe features of the system.

RELATIONSHIP TO OTHER PROJECTS

There is a great deal of current interest among electrochemists in finding ways to control the chemical environments of reacting substances in detail. Work with chemically modified surfaces or with systems involving monolayer assemblies of surfactants deposited by the Langmuir-Blodgett method is almost always motivated by that idea. It shares much in common with our goals, hence we maintain close contact with Professors F. C. Anson (Caltech), A. J. Bard (Texas), T. Kuwana (Ohio State), R. W. Murray (North Carolina), and M. S. Wrighton (MIT), all of whom have extensive work proceeding in these areas.

We are in a virtually unique position in working with assemblies of molecular solids created by vacuum processing and casting techniques. Although the basic technology is readily available, the detailed methods for working with molecular materials have not been developed. Most of the methods used here have been created in our laboratory. Other work with related materials is going on in the laboratories of Dr. J. Fajer (Brookhaven), Dr. F. Kaufman (IBM), Dr. J. Pochan (Xerox), and Dr. M. Gouterman (Washington). We stay abreast of their developments, and they have shown interest in ours.

Exciton propagation and collection have been studied for a long time, but they continue to be interesting specifically within the context of possible antenna systems for photochemical reaction centers. Professors R. Kopelman (Michigan) and R. Silbey (MIT) are active in this area. We watch their work closely and have had opportunities for helpful interchanges with both.

In addition to the general relationships cited above, we are cultivating a specific collaborative effort with Professor David G. Whitten of the University of North Carolina. The details have been discussed in Technical Results in FY 1980.

Another collaborative arrangement involves the analytical service groups of our MRL. We have a continuing interest in being able to characterize our assemblies, and we make steady use of the excellent facilities available here. Because many of the materials of interest to us are not usually found in the form of films, analytical methods for dealing with them are often unavailable. The development of suitable methods therefore involves research, which our group carries out in collaboration with Dr. Peter Williams.

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Ph.D. thesis, Chemical Engineering, R. C. Alkire, adviser (1979)

Lee Warren Wiechmann
An Ellipsometric Study of Salt Film Formation During Passivation
M.S. thesis, Chemical Engineering, R. C. Alkire, adviser (1979)

IMPURITIES IN SUPERCONDUCTORS

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ABSTRACT

We are making electron tunneling measurements on superconducting samples with dissolved hydrogen. The measured superconducting transition temperature indicates whether the hydrogen aids superconductivity. The tunneling data are analyzed in detail to determine the changes in the electronic structure, the phonon spectrum, and the electron-phonon coupling which the hydrogen introduces.

We are also making electron tunneling measurements on simple-metal superconductors with magnetic impurities. The data show directly that the impurity atoms in a sample are associated with a band of bound electronic states. The energy of the band is a direct measure of the strength of the interaction between the magnetic impurity atom and the conduction electrons; this strength is compared with theory and with the results of thermal conductivity measurements which were previously carried out. The shape of the band is compared with theoretical calculations of the effects of the magnetic interaction on the electronic states.

We propose to begin an investigation of the effect of 3d-element magnetic impurities on the upper critical magnetic field H_{c2} of Chevrel-phase compounds. It is hoped that these impurities will substantially increase the already very high values of H_{c2} at low temperatures in the materials.

PURPOSE

The properties of superconductors are affected by impurities. We are investigating the effects of two types of impurities. One type is hydrogen; the other consists of magnetic impurities.

Simple metals (i.e., non-transition elements) are used for the host metals, so that we can analyze the results without having to include unnecessary contributing effects. No previous work of this type has been done for hydrogen impurities. Molecular hydrogen is being used. The magnetic impurities are from the 3d part of the periodic table. In these elements, the magnetic electrons are poorly shielded by intra-atomic electrons, so they interact strongly with the conduction electrons of the host metal. Only a very small amount of previous work has been

done on 3d element magnetic impurities in simple-metal superconductors, other than that which has been performed in our own group.

The principal experimental method which we have been using, tunneling, yields directly the electron density of states. The results for the hydrogen-doped samples are further analyzed to yield the phonon effective density of states.

We intend to begin, in the next fiscal year, an investigation of the effect of 3d element magnetic impurities on the upper critical field of Chevrel-phase compounds. This work will be undertaken when the work on the effect of hydrogen as an impurity is completed.

Hydrogen Impurities

Hydrogen doping has dramatic effects on superconductors. For example, pure palladium, which is not superconducting, can be made to become a superconductor at the comparatively high temperature of 9 K by adding hydrogen, and can be made superconducting at even higher temperatures (up to 16 K) by adding hydrogen with copper, silver, or gold. Similarly, the superconducting transition temperature of aluminum can be increased from 1.3 K to 7 K by introducing hydrogen. Hydrogen also produces anomalies in the thermal conductivity of niobium and tantalum, and in the specific heat of vanadium, niobium, and tantalum in the superconducting state.

These effects are difficult to interpret because there are many contributing mechanisms: (a) a reduction of normal-state spin fluctuations, (b) a change in the normal-state 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. In our experiments, precipitation is avoided, and mechanisms (a) and (b) are negligible because the host metals are simple metals. The data are analyzed by a method which is sufficiently powerful to distinguish between the effects of mechanisms (c) and (d).

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 cold (2K) substrate. (The samples could also be made by ion-implanting the hydrogen, but this method yields a very inhomogeneous sample, so we avoid it.) By performing electron tunneling measurements and analyzing the results using McMillan's method, the phonon and electron densities of states and the electron-phonon coupling constant are determined. The superconducting transition temperature and the resistivity of each sample are also determined.

The data help us to understand in detail 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 and distribution are self-evident.

Magnetic Impurities

The properties of superconductors are strongly affected by magnetic impurities. For technological purposes, an important effect is the shift in the low-temperature critical magnetic field. This shift, although usually downward, can be upward, by as much as 125 kilogauss, if there is an 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 the 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.

We are investigating 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 has, therefore, not been developed in a rigorously correct way. In conjunction with thermal conductivity, specific heat, critical field, and critical temperature data which we acquired previously, we are now obtaining electron tunneling data. The materials are films of indium, lead, and tin, doped with chromium, manganese, and iron. 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 handled, we will have a very complete picture of the fundamental properties of these materials, and the theories which are available (those of Shiba and of Müller-Hartmann and Zittartz) can be tested definitively. Possible lines along which the theories should be improved may be indicated by our results. Furthermore, the strength of the interaction between the impurity atom's magnetic electrons and the host metal's conduction electrons is indicated directly by the experimental results, and this interaction strength can be compared with an ab initio calculation of it by Professor A. B. Kunz of this Laboratory. We believe this is an opportunity to increase our fundamental understanding of the effects of magnetic impurities on metals.

TECHNICAL PROGRESS FY 1980

Hydrogen Impurities

We have acquired a good deal of data, indicating that the superconducting transition temperature of indium is raised appreciably by molecular hydrogen. We have also obtained tunneling data on hydrogen-doped indium. The data indicate a broad band of phonon modes, with energies located in the region between 30 and 90 millivolts. The phonon band has peaks at approximately 37 and 47 millivolts. We are analyzing the data to determine the contribution of these phonon modes to the electron-phonon interaction.

We also have obtained tunneling data on pure lead, and are just now obtaining the data for a hydrogen-doped lead sample. The experiments have generally turned out to be quite difficult, because of the large tunnel-junction bias voltages which must be used to explore electron energies in the neighborhood of the high frequency localized vibrations which are expected for the very light-mass impurity (hydrogen) which is under investigation. In order to bias the junction at such high voltages without heating it up too much, a high-resistance junction must be made, and this is very hard to do; most high-resistance junctions are unacceptable because leakage currents through them dominate the tunneling currents which are of interest, and which decrease exponentially with film thickness. Because of this problem, our progress on this experiment has been slower than we expected. We have decided, therefore, to obtain as much information from this project as we can by next October, and then to direct attention to other matters, which we describe below.

Magnetic Impurities

We have made and successfully investigated another sample of manganese-doped indium to improve the sample quality. By producing a cleaner aluminum counter-electrode for our tunneling measurement, we have, in fact, obtained much better data. The theoretically expected band of impurity-associated states is well defined. We have written and put into operation a computer program for calculating the theoretically expected tunneling curve. The observed band of states is not as sharply defined as the theory predicts if one includes only s-wave scattering of conduction electrons from the impurity atom. However, we have shown how to include higher partial-wave scattering in the analysis, and we have also (under another grant) calculated, with A. B. Kunz, the amplitude of this scattering for the various partial waves. Inclusion of this higher-wave scattering, with the theoretically determined amplitudes, reproduces rather well both the position and shape of the observed band of impurity-associated states. The position of the band is also in good agreement with that which we determined previously from our thermal conductivity data.

We are continuing by investigating manganese-doped lead. To date we have obtained good data on two different samples. (Each "sample" is actually three different tunnel junctions, made simultaneously, to assure reproducibility of the results.) Again, a well-defined band of impurity-associated states is seen, but it is not as well defined as in the indium-manganese samples. We are now calculating theoretical tunneling curves to fit to our data. The a.c. conductance curve for one of the lead-manganese samples is shown in Figure 1. The large peak and dip which occur near 1.24 mV are expected for any tunnel junction between two superconductors, as is the main rise which starts at about 1.56 mV. These features are also seen by us for undoped lead. The rise in conductance located between 1.47 mV and 1.56 mV is the signal that an impurity-associated band of states is present. (The band can also be seen in the I-V curve of the junction, but the dI/dV curve shown in Figure 1 brings it out much more clearly.)

Fig. 1 ac conductance for tunnel junction versus voltage, for a lead-manganese alloy sample.

These are the first observations of this band of states in superconducting alloys which are homogeneous samples, and whose properties can therefore be compared quantitatively with theory.

PUBLICATIONS (Calendar Year 1979):

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Phys. Rev. B19, 1409-1419 (1979)

D. M. Ginsberg
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Phys. Rev. B20, 960-962 (1979)
Also supported by NSF

J.-K. Tsang and D. M. Ginsberg
Electron Tunneling Observation of Local Excited States in Manganese-
Doped Indium
Phys. Rev. (in press)
Also supported by NSF

ULTRASONIC STUDIES OF THE STRUCTURE OF MATTER

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Supporting Agency: U. S. Department of Energy

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ABSTRACT

Dipolar point defects in crystals are under study using ultrasonic techniques. Measurements of attenuation and velocity as a function of polarization, temperature, defect concentration, frequency and annealing temperature are used to obtain symmetries, diffusion parameters and dipole strengths of the defects. Presently under study are impurity-interstitial complexes in aluminum, copper and niobium, hydrogen in niobium, and hydroxyl ions in rubidium chloride. Impurity-interstitial complexes play an important role in the radiation damage reactions in metals, while others are of special interest for study of quantum effects in diffusion.

PURPOSE

Properties of metals containing interstitial atoms and interstitial-impurity complexes and alkali halides containing substitutional impurities are under study using ultrasonic techniques. Measurements of ultrasonic attenuation and velocity as a function of polarization, temperature, frequency, defect concentration and annealing provide information on defect symmetries, binding, rotation and migration energies. The use of sensitive apparatus permits studies at defect concentrations of a few ppm, where the properties of isolated defects can be determined. For metals the phenomena under investigation are basic to 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 and hydrogen in metals. The information obtained 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 as well as for dipolar impurities in alkali halides. A determination of the symmetry of H and D in Nb is of importance in establishing recently proposed quantum models for the behavior of hydrogen in bcc metals and the cause of its unusual mobility.

TECHNICAL PROGRESS FY 1980

Most Significant Results

1. Tunneling of Mixed Dumbbell in Al-Zn. Our most detailed studies of interstitial-impurity dipolar defects are on Al-Zn. We have irradiated specimens containing 0.5, 0.1, and 0.01 atomic percent of zinc in aluminum at 65 K. A defect with $\langle 111 \rangle$ symmetry is found at 103 K which anneals during the measurement, while another with $\langle 100 \rangle$ symmetry is found at 5 K which anneals at 135 K. The measurements for the 5 K peak provide the first strong experimental evidence for the theoretically much discussed and expected caged mixed dumbbell configuration illustrated in Fig. 1. In addition, the

Fig. 1. Schematic view of the mixed dumbbell configuration in the fcc lattice formed by an undersized impurity (shaded atom) and an atom of the host lattice. The axes of new mixed dumbbells which can be formed by dumbbell motion around the corners of the octahedron shown in the figure are indicated by the dotted lines.

surprising result is found that the defect tunnels between the equivalent states. The evidence for the mixed caged configuration arises mainly from the polarization dependence of the diaelastic and paraelastic ultrasonic response of the defect. A large diaelastic effect in C_{44} anneals with this defect, while the paraelastic response occurs entirely in the C' elastic constant, as would be expected for this symmetry.

The evidence for tunneling is obtained by combining ultrasonic attenuation and velocity measurements at 10 and 30 MHz. It is easily shown that the ratio R of $\Delta/\omega\Delta v$, where Δ is the decrement, v is the ultrasonic velocity and ω is the frequency, should be independent of ω for a simple Debye relaxation. Once this test is satisfied, then the ratio R gives the temperature dependence of the relaxation time. The results of such a test are shown in Fig. 2 where R is found to be independent of ω . It is found that the test is satisfied for both 0.1 and 0.5% Zn in Al. The relaxation time is found to be Arrhenius at high temperature and independent of temperature between 2 and 4 K, providing strong evidence for tunneling of the complex. The low temperature increase of the decrement shown in Fig. 3 is not a second low temperature peak, but is just due to the expected increase of the relaxation strength while the relaxation time remains frozen.

Fig. 2. Relaxation time τ derived from velocity and attenuation measurements on irradiated Al-Zn peak 1.

Fig. 3. Annealing of peak indecrement of Al-0.1% Zn peak 1.

Measurements have now also been made for 0.01% Zn in Al. These are more difficult because the background attenuation due to ultrasonic interaction with conduction electrons becomes very large at low temperature in this case. The results have not yet been fully analyzed, but show that the internal stresses arising from the Zn impurities affect the relaxation strengths. Also, for this case saturation effects are obtained when the Frenkel Fair concentration is of the order of the Zn concentration.

2. Interstitial Interactions with Oversized Impurities in Al-Mg. We have obtained the first results for interstitial impurity complexes with oversized impurities, where the theoretical expectation is that mixed dumbbell configurations will not occur. It is found that there are many peaks of differing symmetries but they are much weaker than those found previously for undersized impurities. The results after annealing to 145 K for a specimen with 0.1% Mg are shown in Fig. 4. There are six peaks. Peak 5, not shown

Fig. 4. Peaks found in decrement Δ of irradiated Al-0.1% Mg for C_{44} and C' polarization after annealing to 145 K.

in the figure, anneals out by 80 K. The other peaks all increase in size at 130 K. Peaks 3, 4, 5, and 6 occur in C_{44} , while peaks 1 and 2 occur in C' . Peaks 1 and 4 occur at 19 K at 10 MHz. Peaks 2, 3, and 6 anneal together near 200 K, while peaks 1 and 4 anneal near 220 K. The changes in peak height all correlate well with resistivity changes. The small strength and large number of peaks seems consistent with the general fact that large numbers of weakly bound equivalent binding positions should be available for the interstitial near an oversized impurity. Further experimental and theoretical work is needed to identify the specific defect configurations involved.

3. Defects in Irradiated Al-Fe. Although Al-Zn now appears to be the simplest and best understood system, the Al-Fe system has been the most extensively studied using other techniques (resistivity, channeling, low frequency internal friction, and Mössbauer measurements). The caged mixed dumbbell model was first put forward to account for results for this system, but there now exists serious doubt about the applicability of the model for Al-Fe. Channeling measurements by Swanson gave evidence for $\langle 100 \rangle$ symmetry of the Al-Fe mixed dumbbell. Mössbauer measurements on polycrystals by Vogl and Mansel identified a sudden change in the Debye-Waller factor near 20 K as arising from a caged mixed dumbbell. A peak in low frequency internal friction measures observed by Rehn and Robrock on polycrystalline Al-Fe corresponded well with the Mössbauer results, and all

this evidence was taken together to make a good case for the caged mixed dumbbell model. However, this simple picture failed to account for subsequent internal friction and Mössbauer measurements on single crystals. Rehn and Robroch measured C_{44} , but not C' , and found evidence that the defect had $\langle 111 \rangle$ and not $\langle 100 \rangle$ symmetry. Vogl's single crystal Mössbauer measurement seem to support this result.

We have made measurements on Al-Fe at 10 and 30 MHz and find a relaxation peak near 20 K in both C_{44} and C' . However, these peaks occur at slightly different (~ 1 K) temperatures and also anneal at slightly different temperatures. The defects in Al-Fe are plainly more complex than in Al-Zn. However, since there is an apparent discrepancy between the results for the different techniques, we decided to repeat the measurements. In doing so we have indeed confirmed our earlier result that there are peaks in both C' and C_{44} near 20 K, which anneal at different rates. The configuration of the mixed dumbbell in this system therefore remains in doubt.

RELATIONSHIP TO OTHER PROJECTS

We collaborate with J. Holder of this Laboratory on radiation damage studies, and in this work have support from the group of J. Koehler. The hydrogen in metals project is a collaboration with H. K. Birnbaum. We expect the impurities in alkali halides studies to make contact with related work using other techniques by A. C. Anderson and M. V. Klein. The ultrasonic measurements are unique and are not done at other laboratories, but related work at lower frequencies is done by Rehn at Argonne, Robroch at Julich, Germany and Okuda at the Japanese Atomic Energy Research Institute. An ultrasonic program is being developed by D. Poker at Oak Ridge National Laboratory. We are in close contact with each of these programs.

The principal investigator has support of \$40,000/yr. from the National Science Foundation for research on Dislocation-Defect Interactions in Crystals (NSF DMR-77-10556).

PUBLICATIONS (Calendar Year 1979):

R. D. Isaac and A. V. Granato

A Unified Theory of Dislocation Motion Including Thermal Activation and Inertial Effects

Proceedings of the 5th International Conference on Strength of Metals and Alloys, Aachen, FRG, August, 1979, P. Haasen, et al, eds. (Pergamon Press, Oxford, 1979), pp. 493-498

Also supported by NSF

D. B. Poker, G. G. Setser, A. V. Granato, and H. K. Birnbaum

Low Temperature Anelastic Behavior of Niobium Containing Hydrogen

Proceedings of the International Conference on Hydrogen in Metals, Munster, Germany, March 1979

Z. Phys. Chem. (NF) 116, 439-445 (1979)

MRL SUPPORTED THESES (Calendar Year 1979):

Kenneth Lowell Hultman

Interstitial-Impurity Trapping in Al-Fe and Al-Zn

Ph.D. thesis, Physics, A. V. Granato, adviser (1979)

David Brian Poker

A Low Temperature Ultrasonic Study of Hydrogen in Niobium

Ph.D. thesis, Physics, A. V. Granato, adviser (1979)

DEFECT AND ELECTRONIC PROPERTIES OF SOLIDS

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ABSTRACT

The research program is chiefly directed toward elucidating the basic atomistic mechanisms responsible for mass flow (diffusion) in a wide variety of solids, both crystalline and amorphous, metallic and insulating. Additional studies involve the effects of high hydrostatic pressure on defect and electronic properties of these materials. Current diffusion studies are directed toward resolving the anomalous behavior observed in certain body-centered-cubic transition metals and in finding precise models to describe the extremely rapid mass transport in "superionic" conductors. Principal experimental techniques employed are precision radiotracer measurements of diffusion and isotope effect and (in ionic solids) ionic conductivity as functions of temperature and pressure. Pressure has also been a tool for study of the electronic properties of a number of metallic conductors. Current interest is centered on micro-magnetic and spin-glass alloys and on metallic glasses, which exhibit anomalous magnetic and electrical behavior.

PURPOSE

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; and even non-crystallinity, as evidenced in amorphous or "glassy" solids. 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 change, 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 aliovalent 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 non-randomness 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. Measurements 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 micro-magnetic and spin-glass materials and of amorphous metals ("metglasses").

TECHNICAL PROGRESS FY 1980

Most Significant Results

Work has been completed on a study of the effect of hydrostatic pressure on the ionic conductivity of a wide variety of crystals with the fluorite and related structures: CaF_2 , SrF_2 , BaF_2 , CdF_2 , SrCl_2 , PbF_2 , PbBr_2 , and PbI_2 . Measurements were made for pressures up to 0.6 GPa (6 kilobars) and temperatures up to near the melting point. The activation volumes for extrinsic vacancy motion were obtained from the effect of pressure on the conductivity of doped and oxygen contaminated samples. The formation volumes of intrinsic defects were calculated from measured activation volumes at high temperatures (see Table). The defect volumes were found to be uniformly small and consistent with the dominance of Frenkel defects in all cases except PbCl_2 and PbBr_2 , where large formation volumes were observed, indicating Schottky defects.

ACTIVATION PARAMETERS FOR MATERIALS STUDIED

Material	$\Delta E_m^{\dagger}$	$\Delta V_m^{\dagger} (\text{v or i})^{\dagger}$	$\Delta E^{\dagger}$	$A^{\dagger}$	$\Delta V^{\dagger}$	$V_f^{\dagger} (\text{F or S})^{\dagger}$	$\Delta E_f^{\dagger}$
CaF_2	$0.52 \pm 0.04 (\text{v})$ $0.82 \pm 0.04 (\text{i})$	$2.1 \pm 0.7 (\text{v})$	2.02 ± 0.07	1.2×10^9	7.0 ± 0.5	$9.8 \pm 1.6 (\text{F})$	$3.00 \pm 0.16 (\text{F})$
SrF_2	$0.96 \pm 0.04 (\text{v})$	$3.3 \pm 0.3 (\text{v})$	2.10 ± 0.08	5.8×10^9	7.5 ± 0.5	$8.4 \pm 1.1 (\text{F})$	$2.28 \pm 0.11 (\text{F})$
BaF_2	$0.51 \pm 0.02 (\text{v})$	$3.0 \pm 0.3 (\text{v})$	1.46 ± 0.02	2.6×10^7	5.6 ± 0.3	$5.2 \pm 0.4 (\text{F})$	$1.90 \pm 0.03 (\text{F})$
CdF_2	$0.64 \pm 0.07 (\text{v})$	$3.1 \pm 0.2 (\text{v})$	-----	-----	6.5 ± 0.5	$6.8 \pm 1.1 (\text{F})$	-----
$\beta\text{-SrCl}_2$	$0.37 \pm 0.03 (\text{v})$	$3.5 \pm 0.3 (\text{v})$	1.62 ± 0.03	1.8×10^9	$6.5 (?)$	6 (F)	$2.50 \pm 0.08 (\text{F})$
$\beta\text{-PbF}_2$	$0.25 \pm 0.02 (\text{v})$	$1.75 \pm 0.25 (\text{v})$	0.75 ± 0.03 1.12 ± 0.03	9.6×10^6 2.4×10^9	4.25 ± 0.35 6.5 ± 0.4	$5.0 - 6.0 \pm 0.8 (\text{F})$	$1.11 \pm 0.07 (\text{F})$
$\alpha\text{-PbF}_2$	$0.33 \pm 0.03 (\text{v})$	$2.1 \pm 0.41 (\text{v})$	-----	-----	7.1 ± 0.4	$10.0 \pm 1.0 (\text{F})$	-----
$\alpha\text{-SrCl}_2$	$0.44 \pm 0.02 (\text{v})$	$4.3 \pm 0.3 (\text{v})$	1.08 ± 0.04	-----	7.1 ± 0.4	$5.6 \pm 0.9 (\text{F})$	$1.28 \pm 0.09 (\text{F})$
PbCl_2	$0.32 \pm 0.02 (\text{v})$	$4.7 \pm 0.2 (\text{v})$	1.12 ± 0.04	1.57×10^7	19.8 ± 0.5	$45.3 \pm 1.6 (\text{S})$	$2.40 \pm 0.13 (\text{S})$
PbBr_2	$0.30 \pm 0.02 (\text{v})$	$4.4 \pm 0.6 (\text{v})$	1.00 ± 0.02	5.0×10^7	21.6 ± 0.6	$51.6 \pm 2.3 (\text{S})$	$2.10 \pm 0.08 (\text{S})$
PbI_2 (Low pressure phase)	$0.20 \pm 0.06 (\text{i})$ $0.40 \pm 0.03 (\text{Pb})$	$2.2 \pm 0.5 (?)$	1.45 ± 0.05	-----	6.8 ± 0.6	$9.2 \pm 1.6 (\text{F})$	$2.10 \pm 0.12 (\text{F})$
PbI_2 (High pressure phase)	-----	-----	2.2 ± 0.2	-----	1.4 ± 1.6	-----	-----

$\dagger \Delta E_m$ = activation energy for motion of vacancy (v) or (i) interstitial (in eV); ΔV_m (v or i) = activation volume for motion (cm^3/mole); ΔE = intrinsic activation energy (in eV); $A = (n^{-1} \text{cm}^{-1} \text{s})$ exponential prefactor; ΔV = intrinsic activation volume (cm^3/mole); ΔV_f (F or S) = Frenkel (F) or Schottky (S) defect formation volume (cm^3/mole); ΔE_f = Frenkel (F) or Schottky (S) defect formation energy.

The ionic conductivity of most of these materials showed a complex behavior with temperature. In many cases, four separate regions were found, as indicated in the Figure: (i) extrinsic conductivity, traceable to impurities; (ii)

intrinsic conductivity, dominated by anion motion via vacancies or interstitials; (III) contamination region, increase seemingly related to oxidation and/or loss of gaseous anions; (IV) anomalous region, indicating a strong frequency dependence which may be related simply to interactions at the electrodes or, alternatively, may be evidence of a new bulk phenomenon resulting from many-body interactions, as suggested by Jonscher (this last regime is under further study).

Ionic conductivity of SrCl_2 at atmospheric pressure (BaF_2 is essentially identical). Lower curve is for first heat-up; upper curve is for decreasing temperature. Roman numerals explained in text. Curves are drawn through approximately 500 separate data points.

High pressure phase transitions were found in PbF_2 , SrCl_2 , and PbI_2 , and were studied as a function of both temperature and pressure. The transition temperature is found to increase linearly with increasing pressure at high temperatures for both PbF_2 and SrCl_2 , but considerable hysteresis was found in the transition at low temperatures. The transition in PbI_2 occurs at a pressure of about 0.39 GPa and is essentially temperature independent.

Other Results

First data on the effects of prolonged annealing of Zr samples in the bcc phase prior to deposition of radiotracer in situ (without first cooling down to the low-temperature hcp phase) indicate that dislocations introduced by the phase transition are probably not the primary cause of the well-known anomalous diffusion.

Diffusion coefficients measured in pre-annealed samples are only slightly lower (to within a factor ~ 2) compared to those for freshly-transformed samples. This difference does not appear to be sufficient to account for considerable enhancement found at the low temperature end of the bcc range. Work continues on this system, using both fast- and slow-diffusing tracers, as well as Zr tracer itself.

Measurements have been completed on a study of tracer self-diffusion of Ag^{110} in RbAg_4I_5 in the superionic phase below room temperature and show a change in activation energy at the 2nd-order transition in the superionic phase, consistent with ionic conductivity measurements. Similar studies have been started in AgI , which is superionic above room temperature. Preliminary work is completed for doing a measurement of the isotope effect for diffusion in these systems, to be done by simultaneous diffusion of $\text{Ag}^{110\text{m}}$ and Ag^{105} into samples. The major problem has been in securing Ag^{105} tracer, which is not available commercially. Arrangements were made to prepare the tracer by alpha irradiation of Rh foils at the University of Washington cyclotron; techniques needed for subsequent separation of the Ag tracer by radiochemical methods have now been completed here, and a first batch of tracer has been prepared.

Studies of the effect of pressure on electrical resistance of CuMn mictomagnetic alloys, which were discontinued in FY 1979 on the departure of Dr. M. P. Yuhas, have now been started up again by our visitor from France, Dr. J-L Bocquet. The previous work concentrated on concentrated alloys; the new studies will concern more dilute alloys, approaching the spin-glass concentrations. Similar experiments, possibly also involving Hall effect measurements, will be started on amorphous metals.

RELATIONSHIP TO OTHER PROJECTS

Several aspects of our research program are conducted in collaboration with other principal investigators within MRL and in other departments of the University, but all of our research is funded entirely under this contract. Our studies of superionic solids complement those of M. V. Klein and M. B. Salamon (Physics). We have also collaborated in the past with N. Holonyak (Electrical Engineering) in high-pressure studies of light emitting semiconductor materials. C. A. Wert and P. A. Beck (Metallurgical Engineering) have collaborated in studies of diffusion of bcc metals and in studies of the electronic properties of mictomagnetic alloys. Prior work on dichalcogenide materials has been done collaboratively with F. C. Brown and M. B. Salamon (Physics).

Outside MRL, we have engaged in joint projects with H. Frauenfelder, L. Eisenstein, and others, (Physics) in high-pressure investigations of the kinetics of hemoglobin and myoglobin. We have also engaged in some joint research with D. Turnbull and W. Paul (Harvard University) in high-pressure studies of amorphous metals and semiconductors.

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, 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.

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D. Lazarus

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J. M. Oberschmidt and D. Lazarus

Ionic Conductivity and Activation Volumes in the Lead Halides PbCl_2 ,
 PbBr_2 and PbI_2
Phys. Rev. (submitted to)

J. M. Oberschmidt and D. Lazarus

Ionic Conductivity, Activation Volumes and Frequency Dependent Conductivity
in Crystals with the Fluorite Structure
Phys. Rev. (submitted to)

PROPERTIES OF CRYSTALLINE CONDENSED GASES

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Supporting Agency: U. S. Department of Energy

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Steven V. Marx, Research Assistant

ABSTRACT

Direct structural information about atomic motions and phase transformations in the solid state and about atomic defects can be obtained by neutron and by x-ray scattering techniques. This research program uses such techniques, applied to study either model systems (such as crystalline condensed gases), or systems of possible technological importance (such as A-15 superconductors), or both (solid methane and hydrogen). The model systems include solid noble gases, with current focus upon helium and its isotopic mixtures. For hcp ^4He a study of the momentum density distribution is proceeding, using energetic neutrons from the Argonne spallation source. For bcc ^4He and bcc ^3He thermal vacancy measurements are aimed to elucidate the character of the defects whose motion has associated quantum wavelengths comparable to interatomic spacings. For ^3He - ^4He mixtures, direct x-ray study of phase separation processes is possible for the first time. Also in these mixtures, thermal defect production and interactions present a challenge to existing many-body theoretical treatments of such "quantum crystals." Mixtures of different ^3He concentration are found to exhibit some qualitatively different defect characteristics. Finally, our high-resolution x-ray techniques, developed for study of such systems as solid methane (which shows solid-solid phase transitions associated with changes in molecular orientational order), have proven applicable to resolve some existing questions in A-15 superconductors (V_3Si , V_3Ge) showing complex transitions or unusual thermal expansions.

PURPOSE

The goals of this research are:

- 1) To study atomic momentum distributions in solids by the direct means of scattering of energetic neutrons from the developing new generation of intense pulsed neutron sources. Solid helium is taken as the first case, because for it the kinetic energy content is relatively large and because extensive (and varied) theoretical predictions exist.

2) To obtain quantitative experimental data of accuracy sufficient to provide stringent tests of theories of lattice anharmonicity in electrical insulators. Anharmonicity is important because 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 relevant to energy systems.

3) To determine in several different regimes of isotopic mixture concentration, and of pressure, the nature of thermal and possible ground-state defects in the various solid phases of helium, and to elucidate the mechanisms by which atomic diffusion takes place, in a regime dominated by quantum effects. The crystalline heliums are chosen as model systems exhibiting extremely large effects, systems from which one may learn new insights about atomic mobilities in materials.

4) To apply high resolution x-ray techniques to several systems, including selected A-15 superconductors, exhibiting solid-solid phase transitions or structural transformations.

Solid materials suitable for the present program are, in many cases, crystallized condensed gases for which the phenomena arise in extreme form and better separated from other effects. The phenomena can be precisely studied over an especially large range of physical conditions: factors of more than a thousand 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 total impurity content. Finally, isotopic substitution can be used to separate physical and chemical effects and to probe alternative atomic mechanisms.

To pursue these goals, using these materials, continually requires the invention of new techniques and new types of apparatus. Adaptations of these techniques by other scientists give them the means to carry out research in other areas of materials science.

The intense pulsed neutron source program of Argonne National Laboratory promises an exciting new tool in materials science. Our own research goal is to use chopper spectrometer instruments to study (single-particle) atomic dynamics in solids.

Our second goal, understanding anharmonicity in insulators, has both scientific and technological importance. Applications of solid materials in technology for mechanical construction and also as component elements in solid-state electrical devices, often depend upon the thermal properties of insulating materials. Remarkable advances in the microscopic understanding of anharmonicity have occurred in the last decade. Our own interests in this area include not only thermal expansion studies but also are focussed on phenomena in the immediate neighborhood of melting and over a substantial range of densities, where new insights into the short-range interactions between atoms are accessible.

The third goal, like the second, is a continuation of a long-standing interest. It is noteworthy that many of the properties of solid materials are strongly influenced by the crystalline defects they contain. Such defects are often mobile. 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 in the preparation and use of many solid materials of importance to technology. Recently, interest in quantum manifestations of atomic mobility in solids has grown. Model systems, such as bcc ^3He at low densities, are useful in exploring the full range of volume- and temperature-dependent phenomena over a large range of interatomic interaction strengths.

Experimental methods have been developed, in this research program, 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 with some assurance. The contributions of thermal defects to a variety of physical properties of solids have also been established. The methods are found to be applicable to study of technologically important materials, which may yet be available only in the form of small specimens, for example. Some studies of special samples of V_3Si and of V_3Ge are an initial example.

TECHNICAL PROGRESS FY 1980

Most Significant Results

Investigation of the system of solid mixtures ^3He - ^4He has yielded a rich harvest of results of two kinds: i) phase-separation studies by high-resolution x-ray diffraction, a qualitatively new tool for this "quantum-solid" system, and ii) thermal vacancy properties in several distinctly different regimes of the mixtures.

The technical basis for our success in both these areas has been the design, construction, and development of a new orientable x-ray diffractometer--position sensitive detector system. This system yields measurements from weakly-scattering specimens (such as mm-size H_2 or He crystals) held under unusual conditions of temperature or pressure (such as temperatures down to 50 mK and pressures to 25 MPa). Absolute lattice parameters of helium crystals can be obtained with an accuracy 300 ppm, and measurements of changes in lattice parameter to better than 60 ppm. Bragg diffraction peak widths can be determined, their intensities estimated, and also the crystalline substructure and misorientation (mosaic character) of the specimens simultaneously investigated. It turns out that behavior of these various characteristics is often distinctly different. Having them determined concurrently on a given specimen is a powerful means of achieving progress in elucidating the unusual phenomena appearing in ^3He - ^4He mixtures.

Phase separation has been studied in mixed crystals with concentrations of $x = 51\%$, 28% , and 12% ^3He and melting pressures between 3.0 and 6.1 MPa.

Accurate phase separation temperatures T_{ps} were obtained from shape changes in Bragg diffraction peaks as specimens were cooled. Some typical results are shown in Figure 1. It was found that regular solution

Figure 1. Overall summary of x-ray lattice parameter measurements on a 28% ^3He specimen solidified at 3.475 MPa. The absolute lattice parameter (x) was obtained with 300 ppm accuracy before the cooling run. The circles indicate data upon cooling, and the crosses upon warming. At high temperatures the effect of thermal vacancies is visible (see Fig. 2). Phase separation occurs upon cooling to 395 mK, the most sensitive signature (not shown) being an increase in the Bragg diffraction peak width. The parent phase is bcc and just after separation both the ^4He -rich (lower data) and ^3He -rich (upper data) phases are also bcc, with essentially the same crystallographic orientation. The ^3He -rich phase, upon further cooling, commenced transformation to hcp structure, which is shown by arrest of changes in the bcc lattice parameter. Warming data for this specimen reproduce cooling data fairly well, because the specimen was kept below the phase separation temperature only 5 hours. Obtained separately, and not shown, were useful measurements of crystalline mosaic structure and Bragg peak intensity.

theory accurately describes the relationship of T_{ps} to the critical temperature of phase separation T_c for 51% and 28% mixtures, with dT_c/dP equal -34 mdeg/MPa . (Although these T_c 's are small, lying in the range 300 to 400 mK, the remarkable atomic mobility in solid He permits phase separation phenomena to develop promptly for investigation). Compared to previous experimental work, employing dP/dT , in other laboratories, our x-ray measurements span a wider pressure range, and yield a value of dT_c/dP intermediate in the range of previous determinations (which cover a factor three span, -15 to -46 mdeg/MPa). The apparent linearity of T_c with melting pressure indicates that the excess volume of mixing is independent of pressure, as expected from Mullin's microscopic calculation of phase separation effects. Furthermore, from our work we deduce that the excess volume of mixing is $-0.57 \times (1-x) \text{ cm}^3/\text{mole}$. Mullin's microscopic estimate of the numerical factor was -0.4 .

Totally new is our ability to measure separately the molar volumes of the separated phases (when they are crystalline), to study their structural orientational relationships to the parent mixed phase, and to determine separately the temperatures at which liquid daughter phases appear upon cooling of the separating constituents (which occurs at the lower pressures studied). We find that data obtained upon warming give unreliable signatures of the equilibrium phase boundary. Severe crystalline mosaic, for example, heals over a very different temperature range from Bragg peak width. Doubts are therefore raised about data in the literature which have been obtained on warming.

As can be seen in Figure 2, lattice parameters of the daughter phases are known as a function of temperature. Assumption of regular solution

Figure 2. Thermal vacancy concentration data on a specimen of 51% ^3He having a melting pressure of 3.565 MPa. In a cell confining the specimen to constant macroscopic volume, net changes in vacancy content are given by the x-ray lattice parameter changes $-3\Delta a/a$. Note the extraordinarily large concentrations of vacancies; near melting the vacancies contribute about 20% of the pressure of the solid, a fact unrecognized in previous experimental studies of solid helium mixtures. The vacancy parameters for energy, e_v , and apparent entropy, s_v , are shown. In one case s_v is set at zero. When let free, the fit for s_v indicates that the (complex) net result of the various ^3He - ^4He -vacancy interactions is a non-configurational entropy contribution to the vacancy system near zero. This mixture exhibits phase separation when cooled below 388 mK.

Behavior of the phase separation line (T_{ps} versus s) permits the construction of lattice parameter versus concentration x dependences for the first time. Knowledge of such dependences will be useful for the interpretation of solute-solute, solvent-solute, and vacancy-solvent-solute interactions. But, as described below, more data are required, including direct determinations of pressure changes in the specimens, before such interpretations can be pursued in detail.

Other Results

(i) A report by Dayan and coworkers [Phys. Rev. Lett. **42**, 335 (1979)] of a double superconducting transition in single crystals of V_3Si led to our obtaining such specimens kindly furnished by them. The floating-zone produced specimens had been analyzed at Minnesota by x-ray powder patterns, Auger analysis, metallographic analysis in a secondary-emission monitor, transmission electron microscopy and x-ray fluorescence analysis. The superconducting effects were thought to be intrinsic and not due to the existence of a second phase. The material is silicon-rich, compared to stoichiometric proportions. The results of our high-resolution x-ray study are shown in Figure 3. Intermixed in the specimen are two regions differing in lattice parameter by about 300 ppm. One kind of region is nontransforming and exhibits negative thermal expansion below about 40 K. The other regions transform to tetragonal structure beginning at about 21 K and arresting at about 15 K, corresponding to the lower superconducting critical temperature reported by Dayan and coworkers. There is no overall volume change of the transforming regions, within our sensitivity of 100 ppm.

Because of contradictory results reported elsewhere in the literature, and to pursue the unusual negative thermal expansion of the nontransforming V_3Si a bit further, we have carried out a high-precision x-ray study of

Figure 3. Lattice parameters of a specimen of V_3Si exhibiting a double superconducting transition (Dayan, et.al. 1979). Two types of region were found, differing in lattice parameter by about 300 ppm. The non-transforming region shows negative thermal expansion below 40 K. The transforming region shows essentially no change in unit cell volume upon transformation, which is arrested at about 15 K.

of the negative thermal expansion exhibited by (nontransforming) V_3Ge . Bragg diffraction peak broadening has also been studied in both compounds. This investigation is still in process.

(ii) A cryostat has been constructed to hold specimens of hcp 4He for neutron scattering investigations of the atomic momentum distribution. About one mole of solid helium needs to be constrained, at pressures up to 20 MPa, in a container itself giving minimum neutron scattering, of which the temperature can be well controlled down to about 1 K. Parallel development of the necessary neutron chopper spectrometer system has been proceeding at Argonne National Laboratory. Our scientific collaborators there are Drs. S. K. Sinha and R. K. Crawford. Phasing of the pulsed spallation source with a first version of the chopper was achieved in 1979, but neutron background for the chopper spectrometer instrument remained severe. Installation of a new chopper, and improvement of the neutron shielding in its neighborhood and around the bank of detectors, is scheduled for early March 1980. First runs with the cryostat are scheduled immediately thereafter. The neutron source is ZING-P¹, which should be sufficient to test feasibility of all the apparatus and possibly adequately intense to collect data.

(iii) As this is written early in 1980, construction of our second dilution refrigerator cryostat is not yet complete. Compared to the original machine, with which the results for solid hydrogen and for solid helium were obtained, the new one has larger heat exchangers and a number of practical improvements in the specimen tail. In parallel development and construction is a third-generation position-sensitive-detector system for x-rays which we expect to show improved linearity and stability. Before the end of 1980 these are expected to be in full operation.

RELATIONSHIP TO OTHER PROJECTS

Green's function Monte Carlo methods have been used by Kalos (NYU), Chester (Cornell) and coworkers to obtain momentum density distributions for fcc and hcp He models with Lennard-Jones potentials. Work with other potentials and at finite temperatures, it is hoped, will proceed, for comparison with our neutron scattering experiments. Previous theoretical work by Nosanow and coworkers, by Guyer and coworkers, and others exhibits a variety of predictions to be checked.

Anharmonic crystal studies continue elsewhere at Bell Labs (Fleury, and coworkers, light scattering), at Lawrence Livermore Lab (McMahon, theory), at Rutgers (Horton and coworkers, theory), and at NRC Ottawa (Klein and coworkers, theory).

Experimental studies of solid ^3He , especially of magnetic structures at ultralow temperatures (Adams and coworkers, Florida; Lee and coworkers, Cornell; several European labs), are at the moment loosely related to the present work on low-density ^3He and on ^3He - ^4He mixtures. Diffusion work by NMR techniques by Richards at Sussex, England has been diverted to 2-dimensional studies and at CEA Saclay, France (Bernier and Landesman) to ultra-low temperature melting-line studies. But it is hoped the latter, anyway, will return to the temperature range 200 to 500 mK for ^3He diffusion work soon.

The listing given last year of people and laboratories studying solid-solid phase transitions due to molecular reorientation stands essentially the same except that several are now proceeding to study incommensurate phenomena (e.g., in chain-like geometry) as well.

One can summarize the situation by the statement that we continue to depend upon interest by theorists from a variety of other institutions in the problems we investigate experimentally. This dependence occurs because the theoretical many-body methods themselves have considerable technology associated with their use. On the experimental side, a substantial fraction of our program depends upon use, as collaborators, of a national lab neutron facility, while the rest employs unique apparatus not available anywhere else.

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NUCLEAR MAGNETIC RESONANCE IN SOLIDS

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ABSTRACT

The interests of this group are in fundamentals of solid state physics including many-body problems, phase transitions, magnetism, and solids which possess exotic properties. Most of the present work involves use of nuclear magnetic resonance to probe magnetic and electric fields in solids. As an example, we recently studied what happens to the magnetism of an atom which is normally magnetic (e.g., chromium, manganese, iron) when imbedded in a nonmagnetic metal (copper). By observing the nuclear resonance of copper atoms which are near neighbors to the "magnetic" atom, we have been able to test theories about the electronic structure of the magnetic atom, thereby providing information not previously available. We have begun studies of catalysis, working on Pt-alumina catalysts in conjunction with Dr. John Sinfelt of the Exxon Research Laboratories. We see dramatic differences in the ^{195}Pt NMR as we vary the Pt particle size from 10 Å to 40 Å which reveal the effects of phenomena on the surface on the electronic structure of the Pt particles. We are also currently studying charge density waves in transition metal layer compounds. We make extensive use of special methods such as observing the resonance of one species of nucleus while exciting a second resonance, to enable us to see resonance otherwise too weak to observe.

PURPOSE

I. Catalysis

Heterogeneous catalysis is a process of immense practical importance, but one in which basic understanding is largely absent. A good deal is not known about the nature of the highly dispersed materials of typical catalysts, and important correlations have been found between the catalytic activity or the chemisorption ability and the position of an element in the periodic table. Three quotes from the 1975 article in progress in Solid State Chemistry, by Dr. John Sinfelt of the Exxon Research Labs, one of the leaders of the field, give a flavor of the state of the field.

"It is true that heterogeneous catalytic processes are not generally understood in a detailed mechanistic sense. Moreover, there is no really fundamental understanding of why a given substance is, or is not, a good catalyst for a particular reaction."

"In view of the importance of chemisorption in heterogeneous catalysis, it is obviously desirable to have some understanding of the chemistry and energetics of the relevant chemisorption steps involved. Unfortunately, in the present state of development of the subject of heterogeneous catalysis, there is little that can be said with certainty about the composition and structure of chemisorbed intermediates in any particular case."

"Specificity is perhaps the most intriguing and important aspect of catalysis. Here specificity refers to the ability of a substance to catalyze a particular type of chemical reaction, which is a matter of great practical and fundamental interest. There are few, if any, examples where the factors determining catalytic specificity are understood in detail."

Because of the power for NMR for determining molecular structures, and to study rate phenomena, NMR would appear to be a powerful technique for study of catalysis. The main hindrance is a problem of signal-to-noise ratio -- the number of surface sites on solids is ordinarily so much smaller than the number of sites in the bulk that most surfaces lack adequate numbers of surface atoms even with quite full coverage to permit observation of the NMR of absorbed species. In recent years, there have been great advances in techniques, of magnetic resonance: superconducting solenoids, signal averaging techniques sensitive double resonance methods, methods for narrowing the broad lines of solids, and methods for computer manipulation of data. As a result, we believe one can achieve the requisite sensitivity, and we have undertaken NMR studies of catalysis.

There are many conceivable experiments. We have started with elementary studies so that we can build up knowledge step by step on a firm basis. In the initial work we investigate the nature of the catalyst itself and study the simplest atom, H, on the surface.

To investigate the catalyst it is desirable to examine the NMR of the catalyst itself. We have chosen Pt since the ^{195}Pt nucleus, being spin $1/2$, is free from the complications which would arise if the nucleus had an electric quadrupole moment. Our initial goal is to observe the NMR of the surface Pt atoms.

We are fortunate in having a collaboration with Dr. John Sinfelt, who is providing us with samples. Dr. Sinfelt, one of the 1979 winners of the National Medal of Science, is one of the world's experts on catalysis. He has done extensive work, both chemical and physical, on the Pt-alumina system which he is giving us. In a field such as catalysis, it is vital that potential effects of different sources of catalysts be eliminated.

Slichter has made an analysis of the characteristics to be expected of the NMR of surface Pt atoms. ^{195}Pt in a bulk sample has a large isotropic Knight shift, K_{iso} , arising from the d band through a mechanism called "core polarization." At the surface, this mechanism will produce a different isotropic Knight shift from that of atoms in the bulk. It will also produce an anisotropic Knight shift, K_{anis} , which will broaden the resonance. It is likely also that there will be hybridization of the s and p bands with the d band, which will give an additional isotropic Knight shift. The Knight shift of the valence s electrons in Pt is ordinarily small because the density of states of the s electrons at the Fermi energy is small. However, these same wave functions when admixed in the d band will give much bigger Knight shifts since the d band density of states is much larger. Slichter has estimated the size of the isotropic and anisotropic Knight shifts and the effect of band hybridization using the work of L. Kleinmann on thin films of Ni as a guide. Since the hybridization is thought to be an important feature of the catalytic activity, the possibility of testing hybridization by NMR is very attractive.

A theoretical calculation of band structure for the surface atoms would enable one to do a complete calculation of both K_{iso} and K_{anis} . Thus measurement of these quantities provides a test of a theoretical electronic structure. When a foreign atom is chemisorbed, the bonding will change the Knight shifts. A measurement of the Knight shift would then give information about the chemical bond.

In addition to producing the Knight shifts, the electrons on the Pt will produce spin-spin and spin-lattice relaxation of the Pt nuclei. Measurement of the spin-spin and spin-lattice relaxation times will provide additional information about Pt surface electronic structure.

There are a rich variety of possible experiments involving the nuclei of adsorbed atoms. H^1 , F^{19} , C^{13} are among the nuclei one could study readily since they have spin 1/2 (hence are free of complications of quadrupole moments). Several investigators have observed NMR of H on Pt (Ito et al, Iton, and Bonaret et al), at approximately one monolayer coverage. Aside from changing the temperature, they have not varied the possible parameters very much.

We have begun our research on adsorbed atoms with studies of hydrogen.

II. 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. Our current interest is in charge density waves, and in particular in the so-called commensurate to incommensurate transition.

The particular system we are studying is 2H-TaSe_2 . Above 122K, this system has no charge density waves. Below about 90 - 105K (depending on the sample) TaSe_2 has a charge density wave whose wavelength is an integral number of lattice constants. Specifically, the system is periodic with a smallest unit cell containing 9 Ta atoms and 18 Se atoms. Between 105K and 122K, there are charge density waves but the wavelength is incommensurate with respect to the lattice.

We are studying the ^{77}Se NMR in oriented single crystals of TaSe_2 . This nucleus has a spin $1/2$, and so possesses no quadrupole moment. Since the species is only 7.5% abundant it is difficult to see the NMR. (We have been unable to detect the 100% abundant ^{181}Ta resonance, presumably because of quadrupole strain effects.)

In the commensurate phase, there are three distinct Se sites in the unit cell, each with a distinct Knight shift. As a result, in a sufficiently strong magnetic field, we expect to see three distinct ^{77}Se NMR lines. Data taken by Courturi in our lab at 63 kG confirm this.

In the incommensurate phase, the average wavelength does not match the lattice. McMillan has postulated, however, that this situation arises from a circumstance in which the charge density wave is commensurate over regions of space, with such regions separated by regions of phase slip which he has predicted. We believe we can test his ideas by NMR. The principle is simple. If McMillan is correct, the commensurate regions will give a resonance pattern with three discrete lines. If, however, the wavelength is nowhere commensurate, the structure will be washed out. Suits and Slichter have worked out the theory for the second case. Our goal, then, is to follow the NMR lineshape near the transition to see whether or not we can verify McMillan's concept of discommensuration.

III. Dilute Alloys of Iron Group Atoms in Copper

For several years, we have been investigating 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 using a technique we largely invented and exploited, satellite NMR. We presented a summary of our work, an invited paper at the Magnetism and Magnetic Materials Conference this past summer. We have done theoretical work on a remaining major puzzle collaborating closely with Azevedo, Follstaedt, and Narath at Sandia, whose experiments stimulated our theoretical efforts.

The puzzle first appeared in the temperature dependence of the CuCr total magnetic susceptibility, χ_T which obeys a Curie-Weiss for temperatures above 10K, but deviates strongly for lower temperatures. This result is very surprising since the theories of the Kondo effect, confirmed experimentally

for CuFe, say that a Curie-Weiss law should work well over this temperature range. We have explored a possible explanation which occurred to us when we learned the results of experiments of Azevedo, Follstaedt, and Narath at Sandia on satellites of CuCr at 1K and static fields up to 120kG. These experiments enable them to measure the g-value of any assumed angular momentum J, of the impurity. In essence they observe the saturation moment of the impurity atom magnetization. They found a modest but significant disagreement with our prediction of $g \approx 1$. Stimulated by this work, we made a proposal that seemed to explain their data and to resolve the mystery of the susceptibility. If correct, it gives a further strong confirmation of our general conclusion that Hirst's ionic model is correct.

The essence of our proposal was as follows. Our picture has assigned Cr an effective total angular momentum, J, of 3. We have considered that the $2J + 1 (=7)$ energy levels were degenerate in the absence of an applied static field. If, however, we assume there is cubic splitting of the 7 states (into two three-fold degenerate called states, Γ_4 and Γ_5 , and one nondegenerate state), with Γ_4 lying lowest, we could explain both the susceptibility and the magnetic saturation studies. Ordinarily the existence of a Curie-Weiss rather than a Curie's law is attributed to the Kondo effect. Our calculation shows that for CuCr the mere existence of a crystal splitting gives a Curie-Weiss law at high temperatures.

During the year Abbas, a former member of our group, now at Eastman Kodak Research Laboratory, and Slichter have kept in touch with Azevedo, Follstaedt, and Narath in a give-and-take between theory and experiment to test the possible role of the crystal field we postulated.

TECHNICAL PROGRESS FY 1980

1. Catalysis

Our main effort this year has been devoted to studying the ^{195}Pt NMR of the three Pt-alumina samples supplied by John Sinfelt. We call these samples #4, #5, and #6. Rhodes has measured mean particle diameters of roughly 39 Å, 27 Å and 9 Å respectively using an MRL electron microscope. Figure 1 shows the results of his measurements of the particle size distributions for the three samples.

Until Rhodes got access to the 85kG superconducting solenoid, slightly more than a year ago, we had never observed a Pt resonance in either samples 5 or 6 containing the smaller Pt particles. As soon as we had the supercon in action, Rhodes began searching using spin echoes. To our surprise the resonance of sample #4, which had the largest particles, turned out to be 4.5kG broad, 450 times broader (and thus 450 times weaker) than the ^{195}Pt resonance in bulk metal particles. As a result, substantial signal averaging was necessary even to see the resonance. We encountered several severe instrumental problems with the long signal averaging necessary to see such board lines. The troubles were overcome by special NMR pulse sequence tricks.

Fig. 1 The size distribution for Pt particles in samples 4, 5, and 6. The number of particles, N , within a given size range is plotted against particle diameter D . The solid line is a theoretical curve.

Fig. 2 The integrated ^{195}Pt spin echo intensity versus applied magnetic field, H_0 , for samples 4, 5, and 6. The peak at 84 kG coincides with the position of the resonance in bulk metallic platinum particles. The peak at 80.3 kG coincides with the resonance in a typical diamagnetic Pt compounds. We suspect it arises from Pt atoms in the particle surface layer.

Figure 2 shows the resonances of the three samples. The most notable feature is the dramatic differences in line shape that accompany changes in mean Pt diameter for particles in the size range of typical actual Pt catalysts. A second notable feature is the extreme breadth of the resonances, roughly 4.5kG as contrasted with the 10G width of the NMR in bulk Pt.

There is a strong peak in sample #4 (39 Å particles) at the 84kG, the position of the ^{195}Pt resonance in bulk metals, but there is substantial intensity extending to magnetic fields characteristic of ^{195}Pt resonance in insulators

(~ 80kG). For the two samples with smaller particles the metal peak is gone. We interpret this result by saying that the presence of the surface is felt for distances of approximately 15 Å from the surface.

In sample #6, with the smallest particles, there is a strong narrow peak at 80.3kG, characteristic of insulators. This peak is evident in all three samples but contains a progressively smaller fraction of the line area as the particle size increases. The area under this peak in the different samples corresponds closely to the fraction of atoms on the surface determined by Sinfelt using chemical means. We believe it is likely that this peak arises from surface atoms. Since the peak corresponds to the general location of Pt in diamagnetic compounds, the surface Pt atoms in our sample evidently do not contain unpaired electron spins. At present the samples have oxygen from the atmosphere as their principal surface coverage. We have begun experiments to treat the surface with various chemicals to explore the effects of coverage with other known atoms.

Our results differ dramatically from results of Yu and Halperin on unsupported Pt particles (reported at the March 1979 APS Meeting).

In addition to studying line shapes, Rhodes has measured both spin-lattice relaxation times, T_1 , and spin-spin relaxation times, T_2 at 77K and at 4.2K. He finds T_1 and T_2 at a given chemical shift are independent of sample, showing that each value of chemical shift corresponds to a well defined local electronic structure.

The apparatus Rhodes has assembled will also enable us to look at resonance of a variety of possible adsorbed atoms such as ^{13}C or deuterium but will not work for protons unless we operate our supercon at fields considerably below 85kG, with consequent loss in signal to noise. Rudaz is making good progress in apparatus for use on protons at 360 Mhz corresponding to the full field of the supercon.

Makowka has now built and tested an LSI-11-based computer system for controlling our apparatus and doing signal averaging and other forms of data manipulation. This apparatus, together with a pulse sequence generator built by Dr. Harold Stokes, now is in full time use by Dr. Stokes in conjunction with our old 63kG Westinghouse supercon which we rebuilt this year to achieve a 5-fold decrease in liquid helium operating costs. Stokes is currently studying the magnetic field dependence of the Pt NMR on samples 4, 5, and 6.

II. Transition Metal Dichalcogenide Layer Compounds

In our group Couturié, and now Bryan Suits, have been doing experiments to test McMillan's theory of discommensurations using the ^{77}Se NMR of a single crystal of 2H-TaSe_2 from 4K to above 122K, at a field of 63kG. Couturié has observed changes in spectra as one goes through the different phases. Extensive signal averaging is necessary to obtain adequate signal to noise ratio.

Some of the data is distorted by the need to use a large amplitude of modulation magnetic field. It is possible in principle to correct for the modulation broadening, but there are practical problems with published methods.

Bryan Suits found ingenious ways to overcome the practical problems, invented a generalization of the previous method, and applied the correction to Couturié's data.

The temperature of the commensurate to incommensurate transition is known to be sample dependent. To employ NMR to test McMillan's theory of discommensurations, therefore, requires that we know the transition temperature of the sample under study by an independent means. A year ago a new member of the group, Men Chee Chen, assembled apparatus for detecting the transition by measuring the electrical resistance of the sample, and demonstrated a resistance hysteresis loop associated with the transition as had other workers previously. Efforts to locate the temperature of the transition more precisely came up against limits of our apparatus. Accordingly, Suits has built a new apparatus with greatly improved signal-to-noise and stability characteristic. Preliminary indications are that there is a major hysteresis loop at about 91K, a temperature often assigned to the commensurate/incommensurate transition. If we can show that this is the transition of our sample, our NMR data will confirm McMillan's theory.

We are continuing the resistance studies, and are contemplating other independent means to locate the transition.

III. Dilute Alloys of Iron Group Atoms in Copper

A way of phrasing our theoretical proposal of a crystal splitting of the $J = 3$ state of CuCr is to say that CuCr may possess both a Kondo effect and a crystal field effect, but the question is what is their relative importance. We have tried to fit the data of Abbas at temperatures of 8K and higher and the data of Azevedo, Follstaedt, and Narath at 0.5K to 5K in fields up to 120kG taking the Kondo temperature and crystal field splittings as parameters. Fig. 3 shows a fit to data at 1K assuming no crystal field effect exists, Fig. 4 shows a fit assuming there is no Kondo contribution. Clearly Fig. 4 is a much better fit. We have not been able, however, to fit their data at 0.5K with the same parameters. We have concluded that additional concepts are necessary.

Fig. 3 Data of Azevedo, Follstaedt, and Narath on the satellite shift, DELTA-H , versus ^{63}Cu NMR frequency at 1K (triangles) compared with Abbas and Slichter's theoretical calculation (dashed line) assuming a Kondo effect (Kondo temperature 2.9K, the currently accepted best value) but no crystal field effect.

Fig. 4 Data of Azevedo, Follstaedt, and Narath on the satellite shift, DELTA-H, versus ^{63}Cu NMR frequency at 1K (triangles) compared with Abbas and Slichter's theoretical calculation (dashed line) assuming a crystal field effect but no Kondo effect.

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C. P. Slichter

Satellite NMR in Cu Doped with Transition Impurities
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T. J. Aton, T. S. Stakelon, and C. P. Slichter

The Spin Density Magnetization Near Magnetic Atoms in Copper: CuCr
Phys. Rev. (submitted to)

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Conductivity: Application to Tetrathiafulvalene-Tetracyanoquinodimethane
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C. P. Slichter and H. G. Drickamer

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J. D. Cohen and C. P. Slichter

Model Calculation of NMR Satellite Data for Iron Group Atoms in Copper
Phys. Rev. (submitted to)

PHYSICS OF REFRACTORY MATERIALS - PHYSICAL PROPERTIES OF CERAMIC MATERIALS

Principal Investigator: Wendell S. Williams
Professor of Ceramic Engineering and Physics

Supporting Agency: U. S. Department of Energy

Senior Staff: Wendell S. Williams, Professor

Junior Staff: Craig Allison, Research Assistant
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ABSTRACT

This project seeks to explore the relationship between catalytic activity and chemisorption on the one hand and lattice defects on the other. In particular, powders of "active" tungsten carbide and reference grade WC are under investigation to determine the influence of carbon vacancies on hydrogen chemisorption as assessed by differential scanning calorimetry. A conceptual model of the hydrogen-defect interaction is being developed from previous theoretical studies by A. B. Kunz and co-workers. Electrochemical measurements of the effectiveness of these materials in accomplishing the dual-site dissociation of the hydrogen molecule and release of hydrogen ions into acid electrolyte are also in progress. Extensive characterization of the tungsten carbide powders is being carried out using ESCA, SEM, BET and SAM.

Research on new superconducting materials has focused primarily on the A-15 structure because of the high transition temperatures obtainable. However, The B-1 structure (NaCl) compounds of transition metals and carbon and/or nitrogen have shown transition temperatures as high as 18 K. This project explores the possibility of modifying this limit by exploiting the feature of non-stoichiometry, ordering, and substitution characteristic of this class of compounds.

PURPOSE

This research program has included in its scope a wide variety of properties and phenomena that are characteristic of the transition metal carbides and simpler model materials. These topics include thermal conductivity, electrical conductivity, order-disorder transformations, optical reflectivity, microhardness, dislocation velocity, yield stress, catalytic behavior, microstructure, internal friction, electron energy states, and superconductivity. Although the six materials that comprise this class are generally similar in their refractory character, they exhibit individual differences that can be quite striking. For example, niobium carbide has a superconducting transition temperature of 10 K, whereas vanadium carbide and zirconium carbide, adjacent and above, respectively, in the periodic table, have T_c 's below 1 K. The knowledge base developed from these fundamental studies of a class of similar materials with interpretable individual differences can in time be exploited to create improved materials.

An ongoing project for FY 1980 is a study of the ceramic superconductors NbC_x , an example of B1 (NaCl) structure superconducting compounds with values of T_c that are high enough to justify more intense study for property optimization. Other workers have demonstrated the strong dependence of T_c on the carbon/metal ratio, x , with the highest value of T_c being closest to the stoichiometric composition. The existence of charge density wave in stoichiometric NbC has been proposed in the literature.

After verifying the reported dependence of T_c on x , the project will move to an examination of two ideas that have not, to our knowledge, been explored in earlier work on these superconducting materials. One is the possibility that introducing hydrogen into carbon vacancies in nonstoichiometric NbC_x might raise T_c . From the Russian literature, it is known that such hydrogen doping is possible in this system. The rationale is that the large oscillations expected for hydrogen bound to such a lattice site in a material with a high Debye temperature might enhance phonon-electron coupling. The other idea is the interpretation of the observed maximum in T_c for $\text{NbC}_x\text{N}_{1-x}$ at 18 K for $x = 0.8$ as representing an incipient ordering in the nonmetal sublattice. Such ordering is known for NbC_x when $x = 0.833$, and possibly the lowest energy form of the carbonitride is also ordered. If so, the ordering tendency would be weak in view of the high activation energies for diffusion in these solids, and without long annealing at temperatures around 1000°C the ordering would not be complete. In as much as disorder appears to lower T_c generally, further optimization in this system might be possible.

The other ongoing project for FY 1980 is concerned with ceramic catalysts, in particular, tungsten carbide. Some groups have approached the extraordinary, platinum-like catalytic behavior of WC from the point of view of band theory and have identified similarities in the density of states near the Fermi energy. We have focused instead on the defect properties of the carbides as a class of solids and noted the reported correlation between activity and presence of oxygen impurity and carbon deficiency. The general importance of point defects in providing sites for hydrogen chemisorption is the guiding idea, bolstered by theoretical calculations that were supported by this project and conducted under the supervision of Professor A. B. Kunz of the Physics Department.

TECHNICAL PROGRESS FY 1980

Most Significant Results

Measurements on the superconducting transition temperature of hydrogen-doped niobium carbide have been launched. Sample preparation was a substantial problem, in view of the presence of an oxide film barrier to hydrogen diffusion and the impossibility of making macroscopic foils of this brittle ceramic material (unlike the case of niobium metal). Nevertheless, the technique employed by Birnbaum and others for coating the surface with Pd was used with success on millimeter-thick crystals; specimens were then electrolytically-charged with hydrogen in phosphoric

acid. Another technique, used at IBM for introducing intercalating dopants into layered materials, was also tried, with success: floating the specimen on a mercury pool in the electrolyte allows better electrical contact and advantage can be taken of the hydrogen overvoltage.

An investigation of the superconducting transition was then carried out using a four-probe dc technique and measuring resistivity. Undoped specimens of composition $\text{NbC}_{0.97}$ showed values of T_c of 9.5 K and the width of the transition was 0.5 K. These values are consistent with those reported in the literature. One hydrogen-doped crystal showed a T_c of 8.5 K--a degree lower than that given by the same specimen before electrolytic charging. The normal state resistivity was increased about 10%. The hydrogen content is not yet known, as specimens must be sent to a commercial laboratory--with long delays--for hydrogen analysis. These preliminary results suggest that hydrogen doping will not provide a useful effect in increasing T_c .

Other Results

Experiments to continue the study of hydrogen chemisorption on WC were planned last year. The final result was strong evidence in support of the role of carbon vacancies in the dual-site dissociation of H_2 at a tungsten carbide surface, and theoretical reasons were given to expect such a role in view of the more metallic nature of the local bonding. Since that time, the writer has learned of the existence of a carbon-deficient " W_2C " phase--demonstrated by a Swedish group using neutron diffraction--which could resolve one of the difficulties with the above interpretation: the compound WC is known to exist only in stoichiometric form, and yet the experimental evidence indicated that carbon vacancies are involved in chemisorption. The nonstoichiometric " W_2C " might be responsible as the earlier evidence from United Technologies showed a maximum electrolytic activity at approximately that composition.

Through the cooperation of the staff of the MRL Microstructure Facility (in particular, Mrs. Mochel) preliminary results on grain boundaries in SiC and Si_3N_4 have been obtained in advance of the proposed new subproject. A high-density SiC made by chemical vapor deposition (CVD) by a private company was studied by STEM/XES/EELS and found to have no detectable grain boundary phases. This material is thus unusual, as most polycrystalline SiC contains either SiO_2 or a boride at the grain boundaries as a result of adding sintering aids or from contamination during fabrication. The Si_3N_4 , by contrast, which was hot-pressed, contained tungsten carbide inclusions, MgO at the grain boundaries, and a variety of other debris.

Although the SiC examined in the STEM was chemically pure, the individual grains showed a rich TEM pattern of parallel stacking faults--illustrations of the existence of numerous polytypes for this material.

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PHYSICAL PROPERTIES OF ORDERED AND DISORDERED SOLID SOLUTIONS

Principal Investigator: Helmut Zabel
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Supporting Agency: U. S. Department of Energy

ABSTRACT

Most physical properties depend on the atomic order-disorder in solids. It is, therefore, of great interest to relate these properties to microstructural data. High resolution x-ray scattering experiments are going on to study the pair correlation of interstitially dissolved atoms in quasi two-dimensional systems (graphite-alkali intercalation compounds) as well as in three-dimensional systems (hydrogen in group IV transition metals). The emphasis is on systems exhibiting order-disorder phase transitions, which may range from lattice gas type order-disorder transitions to two-dimensional melting processes by unbinding of dislocation PAIRS. In collaboration with M. V. Klein, the work will be extended to study short range order in binary III-IV semiconductors.

This project is just beginning.

KC-02-02-04 Particle-Solid Interactions

DEFECTS IN SOLIDS

Principal Investigator: James S. Koehler
Professor of Physics

Supporting Agency: U. S. Department of Energy

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ABSTRACT

This research program attempts to understand the behavior of irradiation induced defects in hexagonal and body-centered-cubic metals. Work is continuing on electron induced damage in cadmium, magnesium, zinc and niobium, with emphasis on defect processes that occur at 4 K or below. It is planned that the project will terminate in the fall of 1981.

PURPOSE

The behavior of materials under conditions of external irradiation remains a problem of pressing concern in the search for new and better energy sources. There is an urgent need to understand the production and kinetics of defects introduced into materials by radiation damage because this offers a rational means by which the stabilization of materials in practical service may be planned and the time evolution of the materials manipulated to useful ends. Research funded on this project continues to be focused on the kinetics of defects introduced by electron irradiation at low temperature. A major part of all that is understood about interstitial motion at temperatures below 4 K has been discovered on this project. Processes in the hexagonal and bcc metals are the object of current effort. The project will terminate when the Principal Investigator retires in the fall of 1981.

Our main ongoing effort is to understand the low temperature annealing of pure hexagonal metals. Cadmium has been our first choice of material and significant progress has been made for this metal. Long range interstitial migration is thought to occur during an annealing process found at 2.1 K. We believe that the peaks observed by Coltman and coworkers at higher temperatures arise from impurity related trapping processes.

TECHNICAL PROGRESS FY 1980

In the continuing effort on hexagonal metals our work on cadmium has focused attention on the unusual low temperature behavior of these poorly understood materials. The structure observed between 2.1 K and 2.2 K moves to lower temperature as the dosage is increased. We believe

that this process may involve long range interstitial migration even at these low temperatures. The structures observed at 5 K and above probably arise from impurity trapping or from consequences of the intrinsic anisotropy of hexagonal metals.

Magnesium offers new opportunities for the investigation of defect processes in these hexagonal metals. The results for cadmium indicate that care should be taken to avoid impurity effects. Unfortunately, magnesium cannot be purchased in highly purified form. We are therefore attempting to produce the pure metal by vacuum distillation in order that single crystals of adequate purity may be available for damage studies.

A theoretical investigation has been completed in a different area. We have been calculating the effect of composition modulation in artificially fabricated layered materials. Layers of Au and Al are assumed to lie in 111 planes and to be a few atoms thick. Band structures are then calculated for an infinite stack of layers. We find band gaps developed by the superlattice which can dramatically modify the properties of material. Given modern methods of crystal growth by molecular beam epitaxy, multilayer sandwiches of this type appear to offer a new and exciting method by which the properties of materials can be tailored to predetermined specifications.

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Maria Antonia Menendez

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James R. Bethin

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Ph.D. thesis, Ceramic Engineering, W. S. Williams, adviser (1979)

Larry A. Brey

High Pressure Photophysics of Organic Molecules
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George S. Chryssomallis

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Martin I. Finston

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Harold P. Hjalmarson

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Ph.D. thesis, Physics, J. D. Dow, adviser (1979)
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Kenneth L. Hultman

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Theodore A. Koelsch

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Mechanisms and Dilatancy During the Ductile Deformation of Marble
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Sekyung Lee

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Maria A. Menendez

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Ph.D. thesis, Physics, J. S. Koehler, adviser (1979)

Donald L. Miller

Studies in the Electronic Structure of Matter
Ph.D. thesis, Physics, J. D. Dow, adviser (1979)
(Also supported by NSF and ONR)

David B. Poker

A Low Temperature Ultrasonic Study of Hydrogen in Niobium
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Emanuel P. Roth

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David W. Siitari

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Terry L. Smith

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Michele M. Thomas

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Grant A. Webster

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Lee W. Wiechmann

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Nestor J. Zaluzec

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Philip E. Zapp

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