THE SCIENCE OF MATERIALS

Progress Report

July 1, 1975 - June 30, 1976

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Materials Research Laboratory
University of Illinois
Urbana, Illinois 61801

Report
No. 1198-1/77

April 1976

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Prepared For

THE U. S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
UNDER CONTRACT NO. E(11-1)-1198

~~THIS DOCUMENT IS UNCLASSIFIED EXCEPT WHERE SHOWN OTHERWISE~~
~~TO BE RELEASED TO THE PUBLIC BY THE NATIONAL ARCHIVES~~

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, sub-contractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed or represents that its use would not infringe privately owned rights.

ABSTRACT

This Progress Report contains a description of the basic research and results of ERDA Contract E(11-1)-1198 for the period from July 1, 1975 through June 30, 1976.

Research in Metallurgy and Ceramics included the investigation of the mechanical properties, stress corrosion cracking, and fracture of metals, alloys and transition metal compounds; the investigation of the dynamic structure of water and electrolyte solutions at high temperature and pressure; and the investigation of the properties of oxides and of the magnetic properties of alloys.

Solid state Physics research was focussed on the electronic properties of solids and on defects in crystal structure including radiation damage. Important topics of investigation were the effect of dislocations and impurities on the mechanical properties of metals, diffusion processes in superionic conductors, the defect structure of quantum crystals, high pressure studies of the electronic structure of phosphors, and the magnetic structure of transition metal atoms in nonmagnetic host crystals.

The program is planned to provide an atomic understanding of energy flow, conversion and storage processes and to support with basic research the development of improved materials for energy applications.

INDEX OF ERDA ACTIVITIES 1975-76

Materials Research Laboratory
University of Illinois
Urbana, Illinois 61801

INTRODUCTION	1
LIST OF PROJECT TITLES AND PRINCIPAL INVESTIGATORS.	11
PROJECT REPORTS	13
SUMMARY METALLURGY AND CERAMICS	13
ED-02-01-01-0 Structure of Materials	
Paul A. Beck,	19
Jiri Jonas,	21
C. Marvin Wayman,	28
Wendell S. Williams	32
ED-02-01-02-0 Mechanical Properties	
Carl J. Altstetter,	42
Howard K. Birnbaum	46
Hamish L. Fraser,	53
Marvin Metzger,	58
E. Neville Pugh	61
Charles A. Wert	66
ED-02-01-03-0 Physical Properties	
David A. Payne,	72
Theodore J. Rowland	78
SUMMARY SOLID STATE PHYSICS	82
ED-02-02-02-0 Experimental Research	
Harry G. Drickamer,	87
Andrew V. Granato	95
David Lazarus	99
Ralph O. Simmons	103
Charles P. Slichter	110
ED-02-02-04-0 Particle-Solid Interactions	
James S. Koehler,	119
PERSONNEL	125
PUBLICATIONS,	129
Ph.D. DISSERTATIONS	135
M.S. DISSERTATIONS	136

INTRODUCTION

The Materials Research Laboratory of the University of Illinois is an interdepartmental unit of the College of Engineering organized for the purpose of facilitating interdisciplinary basic research on the properties of materials. Faculty from the Departments of Ceramic Engineering, Chemistry, Electrical Engineering, Geology, Metallurgy and Mining Engineering, and Physics participate in its activities. Policies and procedures of the Laboratory are the responsibility of a Steering Committee composed of Professor C. Wert (Metallurgy), Professor H. Drickamer (Chemical Engineering), Professor N. Holonyak, Jr. (Electrical Engineering), Professor A. Friedberg (Ceramic Engineering), Professor R. Simmons (Physics) and Professor R. Maurer (Physics, Director of the Materials Research Laboratory).

Two Advisory Committees advise the Steering Committee concerning Laboratory programs. The External Advisory Committee is presently composed of Dr. J. Burke (General Electric), Dr. W. Compton (Ford Motor), Dr. M. Nevitt, Chairman (Argonne National Laboratory), Professor A. Overhauser (Purdue University), Dr. R. Oriani (U. S. Steel), and Professor C. Swenson (Iowa State University).

The Internal Advisory Committee, composed of members of the Laboratory, has presently as members J. Dow, C. Flynn, A. Kunz, and M. Salamon of Physics; H. Fraser and E. N. Pugh of Metallurgy; J. Holder of Geology; J. Jonas (Chairman) of Chemistry; and G. Wirtz of Ceramic Engineering.

In addition to these committees, Laboratory activities are assisted by committees for equipment acquisition, the central facilities, health

and safety, and ad hoc program committees for scrutiny of opportunities and direction of the Laboratory's research. These committees are an effective method for promoting interaction between the Laboratory members.

A most important function of the Laboratory is the provision of central facilities for the support of research programs. The major facilities include the Chemical Analytical Laboratory staffed by four professional employees; the Microstructure Facility (transmission electron microscopy, scanning electron microscopy, electronmicroprobe and scanning Auger spectrometer) staffed by two professional employees; the Computer Facility (a Sigma 5 time sharing system with a 96,000 word memory); and a Machine Shop which employs nine machinists. The Laboratory also operates a Storeroom for sale of scientific and metal stock items. The use of these facilities is charged to the Laboratory research projects on a time or job basis as appropriate.

In addition to the major central facilities, the Laboratory supports minor facilities which, while of primary interest to small groups within the Laboratory, are available to all members. These minor facilities include the Optical Laboratory (infrared, ultraviolet and Raman spectrophotometers), the Mechanical Test Laboratory (810 MTS system), the High Temperature Laboratory (vacuum furnaces and dilatometer), the Toxic Materials Laboratory, the Materials Preparation Laboratory (UHV systems primarily for purification of niobium), and the Cryogenics Laboratory (15 stations for cryostats and a helium recovery system).

The primary support of the Laboratory's program is derived from the U. S. Energy Research and Development Administration (Contract E(11-1)-1198 and the National Science Foundation (Grant DMR-72-03026).

Materials Research Laboratory
University of Illinois

The operation of the Laboratory is assisted by the committees and facilities listed below:

Health and Safety

F. Wise, C. Evans, J. Stanley

Machine and Faculty-Student Shop

F. Wise, H. Stapleton

Chemical Analytical Laboratory

C. Evans, C. DePasquali

Toxic Materials Laboratory

S. Brown

High Temperature Laboratory

S. Brown

Magnet Facility

F. Brown, C. P. Slichter

Materials Test Laboratory

C. Altstetter

Microstructure Laboratory (Electron Microscope, Electron Microprobe, Scanning Electron Microscope, X-Ray Laboratory, and Metallograph Laboratory)

C. Wert, H. Fraser, J. Woodhouse

Crystal Growth Laboratory

H. Birnbaum

Accelerator Laboratory (3 MEV Van de Graaff)

J. Koehler

Cryogenic Laboratory

D. Ginsberg

Optical Laboratory (Ultraviolet, Infrared, and Raman Spectrophotometer)

M. Klein

Computer System (Sigma 5)

A. B. Kunz, H. J. Stapleton, V. Metze

Autotrol, Key Punches, Calculators, Typewriters

D. Ginsberg, J. Stanley

Reading Room

R. Maurer

Seminar

R. Maurer

The Professional Staff of the Laboratory are:

Chemical Analytical Laboratory

C. A. Evans, Ph.D., Senior Research Chemist and
Associate Professor, Department of Chemistry

R. J. Blattner, M.S., Research Chemist

J. Baker, B.A., Research Chemist

P. Williams, Ph.D., Research Chemist

Microstructure Laboratory

J. Woodhouse, B.A., Research Microprobe Analyst

I. D. Ward, Research Metallurgist

Accelerator Laboratory

A. Delio, Accelerator Technician

B. Clymer, Accelerator Technician

Computer System (Sigma 5)

V. Metze, Research Programmer

(also, part-time student operators are employed)

Mr. F. Wise, B.A., is Technical Services Supervisor with
responsibility for the Machine Shop and General Storeroom.

Terminated Projects

Paul A. Beck, Department of Metallurgy and Mining Engineering
Electronic Structure and Magnetism of Transition Metal Alloys
Supported by the U. S. Energy Research and Development Administration

New Projects

David A. Payne, Ph.D., Assistant Professor of Ceramic Engineering
Dielectric Solids
Supported by the U. S. Energy Research and Development Administration

Awards and Honors

BECK, P.A., Department of Metallurgy and Mining Engineering
Honorary Membership, Hungarian Physical Society, 1975
Sauer Achievement Award, American Society of Metals, 1976

EVANS, C. A., Department of Chemistry
Scientific Membership, Bohmische Physical Society, 1975

GRANATO, A. V., Department of Physics
Sr. U. S. Scientist - Humboldt Award, 1975

Leaves of Absence

None

Travel

Paul A. Beck, Professor of Physical Metallurgy
August 19 - September 15, 1975 - Budapest, Hungary
Attended Second Specialized Colloque Ampere
Presented invited talk on "Recent Developments in the Magnetism in Alloys" at a meeting of the Hungarian Physical Society and
accepted an appointment to honorary membership in that Society
Visited the Research Institute for Technical Physics of the Hungarian Academy of Sciences in Budapest
Total expenses charged to the contract \$660.73

Ralph O. Simmons, Professor of Physics
September 7 - 17, 1975 - Julich, Germany
Attended International Conference on Dynamics of Molecular Crystals,
presented a paper "X-Ray Diffraction Studies of Methane CH₄ Crystals"
Visited Institutes in Stuttgart and Darmstadt
No cost to the ERDA contract

Visiting Staff Members

M. Amano, National Research Institute of Metals, Tokyo, Japan,
is a Visiting Research Associate Professor of Metallurgy, working
with H. K. Birnbaum, September 1, 1975 through August 31, 1976.

M. H. Loretto, University of Birmingham, England, was a Visiting Research Professor, Department of Metallurgy, May 21 - July 20, 1975, working with H. Fraser.

Y. Lwin, Northern Illinois University at Macomb, spent the summer as a Visiting Associate Professor of Physics, collaborating with the J. S. Koehler group.

Kazuhiro Otsuka, University of Tokyo, is a Visiting Research Associate Professor, Department of Metallurgy through March 4, 1976, working with C. M. Wayman.

Other Visitors

Professor G. Leibfried, Julich, Germany (presently at Oak Ridge National Laboratory), visited the Laboratory, gave a seminar, and discussed irradiation damage with the J. S. Koehler group April 24-26, 1975.

Professor K. Shimizu, Institute of Science and Industrial Research, Osaka University, Japan, visited the Laboratory and consulted with C. M. Wayman, May 11-13, 1975.

Dr. B. D. Nag-Chaudhuri, Vice Chancellor, J. Nehru University, New Delhi, India, visited the Laboratory, consulted with the Director, and gave two University seminars, May 12-15, 1975.

Professor L. Delaey, The Catholic University of Leuven, Belgium, visited the Laboratory and consulted with C. M. Wayman, June 2-3, 1975.

Professor Ulrich Franck, Institute fur Physik, Chemie, Karlsruhe, W. Germany, visited the Laboratory and consulted with H. G. Drickamer on high pressure research, September 22 and 23, 1975.

J. V. Stebut, Centre d'Etudes Nucleaires de Fontenoy-aux-Roses, visited the Laboratory and consulted with the A. V. Granato group October 2 and 3, 1975.

R.G.J. Strens, Department of Geophysics, The University-Newcastle on Tyne, visited the Laboratory and discussed high pressure spectroscopy with H. G. Drickamer, October 15-16, 1975.

John H. Sinfeld, Exxon Corporation Research Laboratory, Linden, New Jersey, visited the Laboratory, gave a seminar, and discussed catalysis with several members of the Laboratory, November 12-13, 1975.

Professor C. Ramasastry, Department of Physics, Indian Institute of Technology, Madras, India, visited the Laboratory and consulted with the Director, November 11-13, 1975.

Professor Wolfgang Hofer, Max Planck Institute fur Plasmaphysik, Garching, West Germany, visited the Laboratory, gave a seminar, and visited the C. A. Evans group October 30 and 31, 1975.

Seminars

MRL Symposium on Superionic Conductors
September 19, 1975

Far Infrared Dielectric Response of Beta Alumina
S. J. Allen, Bell Telephone Laboratories, Murray Hill

Ion-Ion Correlations and Diffusion in Beta Alumina
D. B. McWhan, Bell Telephone Laboratories, Murray Hill

Order-Disorder Transformation in $\text{Rb Ag}_4\text{I}_5$
M. B. Salamon, University of Illinois, Urbana

Diffusion in Superionic Conductors
G. D. Mahan, Indiana University, Bloomington

Surface Sciences Meeting
November 6-7, 1975

Optical Spectra of Adsorbate Atoms
C. P. Flynn, University of Illinois, Urbana

Spectroscopic Studies of Chemisorption and Chemical Reactions on Surfaces
J. E. Demuth, IBM Corporation

Adsorption and Catalysis by Metals: Surface Characterization Using
Photoelectron Spectroscopy and Electron Stimulated Desorption
T. E. Madey, National Bureau of Standards

Electronic Beam Analysis of the Electron Structure of Alloy Surfaces
R. L. Park, University of Maryland

Developing High Resolution, Solid State, NMR for Surface Science
R. W. Vaughn, California Institute of Technology

Adatoms on Metal Surfaces
W. Kohn, University of California

Effect of Physisorption and Chemisorption
C. W. Woo, Northwestern University

Cluster Studies of Surface Electronic Structure and Chemisorption
K. H. Johnson, Massachusetts Institute of Technology

Theory of Photo-desorption
N. Tzoar, City University of New York

Chemisorption Research at University of Chicago
L. Wharton, James Franck Institute

Effect of Alloying on the Mechanisms of Catalyzed Hydrocarbon
Reaction on Metal Surface
G. A. Somorjai, University of California

Studies of Surface Reactions Using Molecular Beam and Auger
Spectrometric Technique

J. B. Hudson, Rensselaer Polytechnic Institute

Molecular Beam Studies of CO/H₂ Reaction on Cobalt and Nickel Surfaces

D. A. Vroom, Intelcom Rad Tech

Desorption of Products Formed by the Interaction of Methanol and
Aluminum Oxide

J. M. White, University of Texas

Photo Catalytic Reaction

M. S. Wrighton, Massachusetts Institute of Technology

Professor Tetsuro Suzuki, Department of Physics, Yokohama City
University, Yokohama, Japan

Martensitic Transformations and Lattice Instabilities

April 8, 1975

Professor P. A. Egelstaff, Department of Physics, University of Guelph,
Ontario, Canada

Three Body Effects in Simple Fluids

April 9, 1975

Professor G. Leibfried, Oak Ridge National Laboratory (from Julich, Germany)

Polarization of Point Defects

April 25, 1975

Professor G. Fritsch, Technical University of Munich, Germany

Measurements of Physical Properties of Sodium Near its Melting Temperature

June 16, 1975

Professor P. C. Gibbons, Princeton University

Electron Energy Loss Spectroscopy

August 8, 1975

Professor Ulrich Franck, Institute fur Physik, Chemie, W. Germany

Properties of Fluids and Fluid Mixtures at High Pressure and High Temperature

September 22, 1975

Dr. F. Dworschak, Julich, Germany

Impurity Interstitial Interactions in Cu and Al

October 15, 1975

Professor Lawrence Slifkin, Department of Physics, University of
North Carolina, Durham

The Role of Ionic Surface Charge in the Photographic Process

October 24, 1975

Professor Wolfgang Hofer, Max Planck Institute fur Plasmaphysik,
Garching, W. Germany

Ion Microprobe Mass Spectrometry

October 31, 1975

Dr. John H. Sinfeld, Exxon Corporation Research Laboratory, Linden, NJ
Catalysis by Metals
November 12, 1975

Professor A. Guinier, Laboratoire de Physique des Solids, Universite
Paris, Orsay
Some New Results in Preprecipitation Studies
November 19, 1975

Dr. Bernd Sonntag, DESY, Hamburg, Germany
Recent Results at DESY
January 8, 1976

PROJECT TITLES AND PRINCIPAL INVESTIGATORS

METALLURGY AND CERAMICS

ED-02-01-01-0 Structure of Materials

Electronic Structure and Magnetism of Transition Metal Alloys

Paul A. Beck, M.S., M.E., Professor of Physical Metallurgy

Dynamic Structure of Supercritical Dense Water and Aqueous Electrolyte Solutions

Jiri Jonas, Ph.D., Professor of Chemistry

Solid State Phase Transformations and Thin Films

C. Marvin Wayman, Ph.D., Professor of Metallurgical Engineering

Physics of Refractory Materials

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

ED-02-01-02-0 Mechanical Properties

Interstitial Solid Solutions

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

Hydrogen Behavior in BCC Metals

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

Applications of Electron Microscopy in Materials Science

Hamish L. Fraser, Ph.D., Assistant Professor of Metallurgy

Deformation of Reinforced Metals

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

The Mechanism of Stress-Corrosion Cracking: Propagation Studies

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

Precipitation in Refractory Metal Alloys

Charles A. Wert, Ph.D., Professor of Physical Metallurgy;
Head, Department of Metallurgy and Mining Engineering

ED-02-01-03-0 Physical Properties

Dielectric Solids

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

Nuclear Magnetic Resonance Studies

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

SOLID STATE PHYSICS**ED-02-02-02-0 Experimental Research**

Use of Very High Pressure to Investigate the Structure of Matter
Harry G. Drickamer, Ph.D., Professor of Chemical Engineering and
Physical Chemistry; Member, Center for Advanced Study

Anharmonic Effects in Solids
Andrew V. Granato, Ph.D., Professor of Physics

Defect and Electronic Properties of Solids
David Lazarus, Ph.D., Professor of Physics

Properties of Noble Gas Crystals
R. O. Simmons, Ph.D., Professor of Physics;
Head, Department of Physics

Nuclear Magnetic Resonance in Solids
Charles P. Slichter, Ph.D., Professor of Physics;
Member, Center for Advanced Study

ED-02-02-04-0 Particle-Solid Interactions

Radiation Damage in Solids
James S. Koehler, Ph.D., Professor of Physics

ED-02-01-00-0 METALLURGY AND CERAMICS SUMMARY

The Metallurgy and Ceramics program of the Laboratory is focussed on the following areas of investigation:

1. The mechanical properties, strength, and fracture of refractory metals, alloys and transition metal compounds. A major collaborative effort exists to understand the effect of gases and light interstitial elements on the properties of niobium, tantalum and vanadium. Emphasis is on the mobility of interstitial solutes like hydrogen, the mechanism of hydrogen embrittlement and fracture in alloys, the precipitation of dispersed phases of hydrides, carbides, nitrides and oxides and the effect of these phases on mechanical properties. An attempt is being made to understand the role of interface parameters in determining the strength of metal matrix-metal fiber and lamellar composite materials.

An understanding is sought of the relationship between the electronic and defect structures of transition metal compounds, like tungsten carbide, and their great hardness, strength, and catalytic properties. Energetic ion sputtering of refractory metal surfaces, a topic of importance for future fusion reactor design, is also being investigated.

These studies are motivated by the importance of improved structural materials that are necessary for applications under extreme temperature and environmental conditions for coal gasification systems, energy systems involving pipeline transmission of gases containing H_2 or H_2S , possible energy storage in the form of hydrides and fission and fusion reactor applications.

2. The dynamic structure of water and its electrolyte solutions under extreme conditions of temperature and pressure is being determined. A byproduct of this research will be information concerning the corrosion of metals under extreme conditions. In conjunction with this research, the relationship between the structure of passive films on metals and alloys and the mechanism of their corrosion under conditions of fluid flow and particle erosion will be investigated. The motivation of this research is its usefulness for the materials problems of geothermal energy utilization, desalination technology, and reactor systems. The feasibility of a practical isotope separation process for ${}^6\text{Li}$ - ${}^7\text{Li}$, using a high temperature, high pressure electrolyte system, will be determined.
3. The electronic and defect properties of oxides, like the La-Co-O system, are being explored from the perspective of their potential applications to catalysis, fuel cells and solar energy. New piezo and pyroelectric dielectrics are being synthesized and their properties determined in an effort to extend the capabilities of these materials as thermal sensors and electric generators. Present materials have unfortunate low temperature limits.
4. The magnetic properties of the micromagnetic (spin glass) systems of 3d transition element metal alloys have been investigated in a program terminating with FY76 because of the retirement of the principal investigator, Professor Paul Beck.

A wide range of experiments have been concluded in alloys of refractory metals. They include confirmation of quantum mechanical tunneling in diffusion of hydrogen in Nb. This experiment by the group

working with Professor H. Birnbaum provides verification of the diffusion theory of Professor C. P. Flynn and Dr. A. Stoneham. The solubility and chemical potential of oxygen in vanadium has been determined by Professor C. Altstetter. Mechanisms of control of alloying elements K, Al and Si during fabrication of tungsten filaments has been determined by Professor C. Wert in collaboration with a research team from Westinghouse. These elements produce arrays of potassium-filled voids during recrystallization which improve the creep resistance of tungsten. The formation of V_2H in vanadium has been shown by Professor M. Wayman to be similar to a conventional martensitic transformation in habit plane, orientation relationship and lattice strain.

Stress corrosion cracking of alloys of magnesium and aluminum has been found by Professor E. N. Pugh to have many similarities to fracture in refractory metals containing hydrogen. Fracture surfaces, both intergranular and transgranular, contain a brittle layer of magnesium hydride. Formation of these stress-induced hydrides is similar to the process of fracture in niobium containing hydrogen found earlier by students of Birnbaum. Further, fracture in a Ti-Al-Mo-V alloy has been shown to be caused by formation of titanium hydride. The hydrogen appears to enter in the β -phase and forms the brittle hydride in the α -phase at the α - β interface.

Age hardening in Cu-Be alloys has been shown by Professor T. Rowland to proceed with the initial formation of coherent precipitates of the compound CuBe which are so small that they have not been detected by electron microscope techniques.

Stacking faults in silicon have been shown by Professor H. Fraser to permit displacement of Si atoms by energetic electrons with energies

significantly smaller than expected. Professor Metzger has shown that the matrix reinforcing phase interaction in metal composites is dominated by interface strain compatibility requirements. Stress strain behavior and ductility dependence on temperature were controlled by the availability of slip modes that met this constraint.

Theoretical calculation of Professor W. Williams and his coworkers of energy levels and electronic wave functions have revealed significant clues to the simultaneous existence of great hardness and metallic conductivity in the transition metal carbides.

The self-diffusion coefficient of the proton and deuteron in water has been determined by Professor J. Jonas from 10°C to 200°C and from 1 to 10 kbar. Apparatus to extend the measurements to 850 K has been constructed.

In the process of synthesizing piezoelectric and pyroelectric ceramics, Professor D. Payne has discovered that the use of $\text{Pb}_5(\text{Ge,Si})_3\text{O}_{11}$ as a liquid wetting agent for the sintering of BaTiO_3 - $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ ceramics reduces the sintering temperature from 1400°C to 750°C with both energy and precious metal conservation over previous procedures.

Emphasis during the coming year will continue to be placed on problems of hydrogen diffusion in the refractory metals and the mechanism and property changes associated with hydride precipitation. Experiments on hydride precipitation in Nb-H will be extended to include spinoidal decomposition at the miscibility gap. Different aspects of this work will be carried out cooperatively by Professors H. Birnbaum, H. Fraser, T. Rowland, N. Pugh, and A. Granato. The new and important project of the extension of the research of hydrogen mobility in the refractory

metals to the investigation of helium mobility will be begun.

The investigation of oxygen-solute interactions in V-Nb-O systems will be completed by Professor C. Altstetter during the next year. An attempt will be made by Professor C. Wert to obtain high temperature strengthening of V-Nb-Ti-Cr alloys through precipitation of submicron coherent particles of mixed carbides. Stability ranges of these particles will be determined.

The investigation of stress corrosion cracking of Mg-Al alloys will be extended by Professor N. Pugh to include the Mg-Al-Zn alloys. In cooperation with Professor H. Fraser he will also examine the effect of iodine on the fracture of Zr alloys--a problem of interest because of the effect of iodine fission fragments on the properties of Zircalloy fuel cladding of nuclear reactors. Stress corrosion cracking of titanium will be investigated by Professor R. Alkire.

Professor M. Metzger's studies of composites will concentrate on the relationship between flow stress and interlamellar spacing in $\text{Ni}_3\text{Al-Ni}_3\text{Nb}$ alloys. Creep enhancement of refractory metals under ion irradiation will be examined by Professor C. Altstetter.

Professor W. Williams' studies of the transition metal carbides will concentrate on the catalytic activity of tungsten carbide surfaces in the oxidation of hydrogen in fuel cells. The dependence of catalytic activity on lattice and surface defects (carbon vacancies) is a primary topic for study.

The research on oxides and dielectric solids of Professor G. Wirtz and D. Payne will concentrate on hydrothermal growth of Bi_2WO_6 , sintering of the $\text{BaTiO}_3\text{-PbGa}_2\text{O}_{11}$ system, evaluation of these and similar compounds

like $\text{Ba}_2\text{TiSi}_2\text{O}_8$ and PbTiO_3 for favorable piezo and pyroelectric properties, growth of Tl_2O_3 , LaCoO_3 and LaCoO_4 crystals, the obtaining of pertinent phase equilibrium information and the determination of data needed to evaluate potential usefulness of LaCoO_3 for the oxidation of CO to CO_2 by water with the production of hydrogen and the usefulness of oxide films to improve solar energy collectors through an enhanced "greenhouse" effect.

The experiments on the structure of water at high temperature and pressures will be extended to 850°C and include measurements on LiCl dissolved in supercritical compressed steam. If the data obtained indicate feasibility, a small system for separation of ^6Li and ^7Li isotopes will be constructed. In parallel with the work on electrolyte solutions, the structure of disordered "plastic" organic solids and polymers will be examined.

The program on corrosion of Professor R. Alkire will be initiated with an investigation of the effect of fluid mechanics on the breakdown of passive layers through particle impaction and cavitation. The experiments will study the effect of controlled impaction as a function of surface shape and electrochemistry. An attempt will be made to explain the dissolution of foreign sulfide inclusions in passive surfaces.

ED-02-01-01-0 Structure of MaterialsElectronic Structure and Magnetism of Transition Metal Alloys

Principal Investigator: Paul A. Beck, M.S., M.E.
 Professor of Physical Metallurgy

Supporting Agency: U. S. Energy Research and Development Administration

Senior Staff: Paul A. Beck, Professor

Junior Staff: Robert D. Shull, Research Assistant
 Randal W. Tustison, Research Assistant

Object: This project has had the specific goal of a better understanding of the magnetic properties of alloys of the 3d transition metals and a general objective of contributing to our knowledge of magnetism. Research efforts have emphasized the effect of the local atomic environment on the magnetic moment associated with a 3d metal atom and the magnetic structure of mictomagnetic or "spin glass" alloys. These alloys occur more commonly than has been suspected among atomically disordered solid solutions. The basic research of the project is relevant to the efficient use of electrical energy devices including motors, generators, and transformers and has implications for the development of computer memories.

Results, FY 76: It has been found that the low alternating field susceptibility at the temperature of the cusp of $\text{Cu}_{75}\text{Mn}_{25}$ is significantly decreased by severe plastic deformation and that the steady field susceptibility in the temperature range of 140-300 K can be accurately fitted to the formula $\chi = \chi_0 + C/(T - \theta)$. Following Kouvel [J. S. Kouvel, J. Phys. Chem. Solids 21, 57 (1961)], the value obtained for C was interpreted on a model involving compensation in the deformed alloy of about 50% of the Mn atomic moments by means of antiferromagnetic interaction between the spins on nearest neighbor Mn atoms, as compared with compensation of only about 25% of the Mn atomic moments for the same alloy in the quenched state. New measurements on severely cold-worked alloys $\text{Cu}_{50}\text{Mn}_{50}$, $\text{Cu}_{40}\text{Mn}_{60}$, and $\text{Cu}_{34}\text{Mn}_{66}$ indicate that increasing the Mn content further increases the fraction of Mn atoms with spins compensated. The results also show that χ_0 increases with the concentration of compensated Mn moments, but that the mictomagnetic freezing temperature, T_f , which has a maximum at ~ 40 at.% Mn, is directly related to the concentration of uncompensated Mn moments.

The Fe-Al alloys with 25 to 32 at.% Al, ordered to the Fe_3Al structure, have very unusual magnetic properties. It was found that the alloys with 28.5 to 30% Al, which are ferromagnetic at room temperature, become mictomagnetic on cooling to ~ 70 to 90 K. Alloys with 30.5 to 45% Al, which are paramagnetic at room temperature, also become mictomagnetic on cooling. The mictomagnetic freezing temperature, T_f , decreases with increasing Al content.

Results Expected, FY 77: Support for this project will terminate with FY 76 because of the retirement of the principal investigator, Professor Paul Beck.

Relationship to Other Federally Funded Projects: The research is carried out with detailed attention to the large amount of work on magnetic systems, particularly in the ERDA national laboratories. Collaboration has existed, also, with the work at the von Laue-Langevin Institute at Grenoble, France with investigators at Strasbourg, France, Amsterdam, Holland and UCLA, Los Angeles. Reciprocally, the importance of the project's work has been recognized by others through the election of the principal investigator to membership in the Hungarian Physical Society in 1974, the receipt of the Hume-Rothery Award of the Metallurgical Society of the AIME in 1974 and the receipt of the 1976 Sauveur Award of the ASM.

Publications: (Calendar Year 1975)

Paul A. Beck and C. P. Flynn
Interpretation of the Susceptibility of Paramagnetic Nickel
Solid State Commun. 18, 127-130 (1975)
Also supported by NSF

A. Mukhopadhyay, R. D. Shull, and Paul A. Beck
Relaxation and Magnetic Clusters in Mictomagnetic Cu-Mn Alloys
J. Less Common Metals 43, 69-82 (1975)
Also supported by NSF GH-37568X and JLCM 43(1975)69-82

R. D. Shull and Paul A. Beck
Mictomagnetic to Ferromagnetic Transition in Cr-Fe Alloys
AIP Conf. Proc. 24, 95-96 (1975)

M.S. Theses: (Calendar Year 1975)

None

Ph.D. Theses: (Calendar Year 1975)

None

Dynamic Structure of Supercritical Dense Water and Aqueous Electrolyte Solutions

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

Supporting Agency: U. S. Energy Research and Development Administration

Senior Staff: Jiri Jonas, Professor
John W. Linowski, Research Associate (Term 1/31/76)

Junior Staff: Michael A. Fury, Research Assistant

Object: A study of the dynamic structure of various materials under extreme conditions of high pressure and temperature represents the main theme of our research. Our interests currently focus on investigating molecular motions, transport properties, and interactions at molecular level in compressed supercritical water, heavy water and compressed supercritical aqueous electrolyte solutions. In addition, we are also studying various organic solids with high degree of reorientational disorder and several specific polymeric systems. The improvement of our understanding of the dynamic structure of the above materials is of both theoretical and practical significance.

The main techniques we currently use are the nuclear magnetic relaxation measurements and NMR self-diffusion measurements. The NMR spectroscopy provides a powerful tool for investigation of molecular motions and interactions at molecular level. One can obtain angular position and angular momentum correlation times for single molecules, and from the measured self-diffusion coefficient via the spin echo field gradient technique, one learns about behavior of linear momentum in fluids. The capability of high resolution NMR spectroscopy via the Fourier transform approach represents an important, unique feature of our experimental setup. In order to extend the information content of our studies, we have recently started using laser Raman spectroscopy to obtain the time dependence of the correlation functions which characterize in detail the motions at the molecular level. In the last several years we gained considerable expertise in high pressure, high temperature NMR techniques, and as far as our current instrumentation is concerned, there is no other laboratory in the USA and/or abroad with the comparable performance features of the NMR experimental system.

Due to our recent progress in NMR instrumentation for work at high pressure and high temperature, we are in a position to study the behavior of compressed water, heavy water and aqueous electrolytes well above its critical temperature. Compressed supercritical water exhibits a number of very interesting properties. The highly compressed supercritical water exhibits typical liquid properties but it has unusually high fluidity and conductivity. It is worth emphasizing that the conductance of water at high pressure and high temperature nears that of concentrated alkali salt solutions. Similarly, under these extreme conditions strong electrolytes may be associated to form ion pairs and then behave as weak electrolytes. We plan to study the details of molecular motions and transport properties in supercritical dense fluids and explain theoretically their unusual behavior.

There are a number of practical aspects to our experiments highly relevant to ERDA's practical energy mission. There has been an isotope enrichment process proposed using high-pressure supercritical steam as a medium for dissolving ionizable inorganic salts and then using the steam solution in an electrolytic cell with countercurrent flow. The efficiency of the isotope separation is considerably enhanced when superheated compressed steam is used as a solvent medium. This process is under consideration and evaluation by the Oak Ridge National Laboratory. Since the major problem in the electromagnetic separation of isotopes is the need for handling large quantities of feed materials with unwanted isotopes, even only a pre-enriching, relatively inexpensive process would be highly desirable. We intend to carry out a theoretical feasibility study for this isotope separation process and if proved encouraging, we shall build a laboratory setup to show the practicality of such an approach. In our planned experiments we shall concentrate on ^6Li and ^7Li isotopes for the following reason. Lithium is used in the primary reactor cooling systems of pressurized water reactors. Highly enriched ^7Li is desirable since it converts to nonradioactive helium upon neutron capture whereas ^6Li converts to tritium. If our experiments on lithium prove successful, then we may attempt a more difficult separation of the isotopes of uranium.

One should also mention some other practical aspects of our experiments which have direct relevance to non-nuclear energy sources. Better knowledge of the properties of water and aqueous electrolytes at high temperatures and high pressures will contribute to the solution of practical problems related to e.g., power generation by steam turbines, geothermal energy utilization, evaluation of certain proposals for underground power production, desalination technology. There is one additional practical aspect of our studies. Supercritical dense aqueous electrolytes are highly corrosive and therefore, during our experiments, we shall gain valuable expertise about corrosion of various materials under extreme conditions of temperature and pressure.

Another aspect of our research activity is the investigation of the dynamic structure of disordered organic solids which exhibit a high degree of reorientational disorder. The goal of these experiments is to learn about diffusion in these disordered materials, and, in particular, to improve our understanding of order-disorder transitions. Our recent experiments on

several so-called plastic crystals indicated that NMR relaxation experiments both in the laboratory and rotating coordinate frames are well-suited to study the nature of these order-disorder transitions. The use of pressure as an experimental variable in studying these disordered materials greatly increases the information content of the NMR experiments. We plan to interpret our experiments in terms of available theoretical models with special emphasis on hysteresis phenomena accompanying these order-disorder transitions. The results will be of importance for theoretical understanding of the important phenomenon of order-disorder transition which is relevant to development of better engineering materials. Since future electronic devices may be based on organic solids, this fact represents another long-range practical aspect of our experiments.

Another class of materials under study are various polymeric materials e.g., polytetrafluoroethylene, polyamides, polyethylene. We plan to investigate molecular motions in these polymeric materials using the techniques described above. Since many practical uses of polymers involve the presence of mechanical forces, our experiments directly relate to the problem of the structure of polymers and their mechanical properties. Of particular interest are polymers which are used as solid lubricants and high temperature polymers. Our studies will help to answer questions such as: What is the molecular structural basis and dynamic phenomena determining the use for a particular polymer as a solid lubricant; what is the high temperature limit of practical uses of special high temperature polymers when under mechanical stress and what is the molecular basis for this behavior? Our results will be useful for laboratories developing new types of polymeric materials.

Results, FY 76:

Most Significant Accomplishments: The self-diffusion coefficients, the proton and deuteron NMR spin-lattice relaxation times in water and heavy water were measured as a function of pressure and temperature in the range 10°C to 200°C and 1-10 kbar.

Analysis of our experimental NMR relaxation data leads to several important conclusions about the motional behavior of water molecules in compressed liquid water and heavy water. First, the initial increase in density at low temperatures produces a faster reorientation of the water molecules. This is easily understood in terms of a simple physical picture. Since reorientation of water molecules must proceed via breaking and reforming of hydrogen bonds, one can readily see that high compression which distorts, disrupts, and generally changes the optimal tetrahedral hydrogen bond network will facilitate such reorientational processes. Second, compression results in a decreased coupling between the rotational and translational motions as reflected in the relationship between the reorientational correlation time of water molecules and shear viscosity. Therefore, the Debye equation fails to describe the effect of density on the reorientation of water molecules. Third, we find that the activation

energies for relaxation, self-diffusion and shear viscosity decrease with increasing density, again reflecting the changes in hydrogen bonding upon compression. From these findings we concluded that compression of water produces major changes in the random hydrogen bond network with the result that water begins to behave more as a "normal" liquid under high compression. Our experimental results are in agreement with recent molecular dynamics calculations on water by Stillinger and Rahman (Bell Telephone Lab., Argonne National Laboratory). In a general sense, the results of these studies can be regarded as a good illustration of the importance of using pressure as an experimental variable in studies of the dynamic structure of liquids. The results of these studies will be published in a series of articles in the JOURNAL OF CHEMICAL PHYSICS.

Other Results: (1) As a first stage of our work on supercritical compressed water, we built and tested an internally-heated, argon pressurized NMR probe which enables us to reach temperatures of 850°K and pressures up to 2 kbar. NMR relaxation and diffusion measurements are in progress.

(2) In continuation of our studies of applicability of hydrodynamic equations at molecular level, we investigated the applicability of the Debye equation which gives the relationship between the reorientational correlation time and shear viscosity. Similarly, as we found earlier for the Stokes-Einstein equation, a modified Debye equation well represents our experimental data on polyatomic molecular fluids.

(3) Using the Fourier transform technique, we obtained unique information about the dependence of the proton chemical shift in water upon density and temperature. A special coaxial sample cell for an external standard which permits measurements at high pressures was developed. The behavior of the proton chemical shift in water with density is in agreement with our other results for water as mentioned above. At low temperatures below ~ 30°C the increased density disrupts the well-developed hydrogen bond network. At high densities the hard core repulsive interactions begin to dominate over the directional interactions which are mainly responsible for the open structure of liquid water at low temperatures and pressures.

(4) In order to investigate diffusion and slow motional processes in disordered organic solids and polymers, we developed instrumentation for the NMR relaxation experiments in the rotating coordinate frames. An exploratory study of a molecular organic solid of cyclohexane was finished.

(5) We have started a theoretical feasibility study of the countercurrent flow electrolytic process for separation of isotopes using high pressure supercritical water as a solvent medium for ionizable salts.

Results Expected, FY 77: We expect to complete our experimental work on water and heavy water up to temperatures of 850 K and analyze the NMR relaxation and diffusion data. The large increase in the ionic product of water at high temperatures and pressures, the question of the extent of hydrogen bonding under these experimental conditions are a few of the many interesting problems we hope to explain on the basis of our experimental

data. We predict that at high temperature and pressure the hard core repulsive interactions between the water molecules dominate over the highly directional forces due to hydrogen bonding. It is likely that the modified Enskog theory which forms a basis for the hard sphere model of fluids may prove successful in interpretation of the experimental data.

At the same time, measurements of LiCl dissolved in supercritical compressed steam should also be completed. The nature of hydration of ions and the extent of ion pairing under these extreme conditions are main goals of our investigation. Additional salts such as KCl, NaCl, CaCl_2 , CaCl , CaCl_3 dissolved in water and/or heavy water will also be studied in the supercritical dense region. Effects of various types of ions on transport properties of ions and water molecules, and on the dynamic structure of these electrolytic solutions will be followed. We expect that the results of these experiments will be interesting and valuable to the extent to justify further instrumentation effort to develop equipment which will allow us to extend our measurement range to temperatures in excess of 1200 K and pressures up to 5 - 10 kbar.

In the case that our theoretical feasibility study for the isotope separation process using superheated compressed steam as a solvent proves promising, we intend to build a small scale laboratory setup to attempt the separation of ^7Li and ^6Li isotopes. If our experiments on separation or enrichment of lithium isotopes are successful, we hope that the Oak Ridge Laboratory will further study the process or we shall extend our work to the separation of isotopes of uranium of mass 235 and 238 using uranium sulfate solutions.

Our preliminary results on the hysteresis effects accompanying the order-disorder transitions in organic solids of adamantane, 2,2,2-bicyclo-octane and hexamethyldisilane indicated the possibility of using NMR relaxation measurements to study the dynamics of an order-disorder transition. First, we plan to carry out detailed experiments on adamantane powders following the time dependence of formation of either the tetragonal brittle phase in the plastic phase or the reverse process by changing the external pressure at constant temperature. We also want to extend these experiments to single crystals and obtain information about anisotropic interactions in these solids. We would like to carry out both isothermal and isobaric experiments. We shall interpret our experimental data in terms of available theoretical models (for example, models based on compressible Ising lattice) for order-disorder transition and plan direct collaboration and/or interaction with theorists in the Materials Research Laboratory at the University of Illinois. In this connection we shall use the NMR relaxation experiment in the rotating coordinate frame to obtain information about the diffusion mechanism in these disordered materials. We are interested in finding whether diffusion in these materials can be interpreted in terms of a simple physical picture and to what extent the detailed molecular structure affects the diffusion mechanism when going from one molecular solid to another.

We have already carried out some NMR relaxation experiments on polytetrafluoroethylene over a wide range of pressure and temperature. Our interest was focused on the dynamic structure of a high pressure phase of polytetrafluoroethylene which was recently discovered. So far our results were not

conclusive and therefore we would like to use the NMR relaxation experiments in the rotating coordinate frame to characterize the molecular motions in this high pressure phase of polytetrafluoroethylene. These studies are of high practical interest because of the widespread use of teflon as a solid lubricant with excellent frictional properties.

We would like to start our experimental work on NMR relaxation experiments on solids using pressures up to 50 kbar. This project will be carried out in direct collaboration with H. G. Drickamer, Professor of Chemical Engineering and Physical Chemistry.

Results Expected, FY 78: In 1978 we expect to continue our work in the three main areas: supercritical dense fluids, disordered solids and polymeric materials. The study of the dynamic structure of various electrolytes in the supercritical dense region should be completed during this period. We expect that the various observed phenomena of theoretical and practical interest will warrant extension of our studies in two directions. First, we would like to start experiments on ternary systems such as water-electrolyte-hydrocarbons; water-CO₂-electrolyte systems or ammonia-water-electrolyte systems. Second, we would like to extend the upper temperature and pressure limit of our experiments to permit work on transport properties and dynamic structure of fused salts. With current interest in the potential use of fused salts as heat transfer media in nuclear reactors, the importance of improving our understanding of these materials is quite obvious. We would like to systematically measure a number of fused salts, including, e.g., a study of transport properties of BeF₂.

In 1978 we expect to have available the equipment for NMR relaxation experiments at pressures up to 50-100 kbar. This opens many new directions of research. To name only one example--the study of the dynamic structure of a high pressure phase of polyethylene and a systematic study of motional dynamics in various other polymeric systems under high pressure.

Depending on the results of our NMR experiments on polymers, we may develop new instrumentation using the Fourier transform techniques to measure NMR spectra of ¹³C at natural abundance in various polymers under high temperature and pressure. The basis for these experiments is the observation that narrow NMR lines are observed in the ¹³C spectra of solid elastomers for temperatures above the glass transition temperature. These ¹³C lines are more than one order of magnitude narrower than proton NMR lines of the same system and are sufficiently narrow to permit resolution of the resonances of individual carbons. The ability to measure the relaxation times of each individual carbon will permit detailed evaluation of segmental motions in various polymers and characterize the relative significance of thermal and volume effects on the dynamics in these materials.

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

We plan to provide our data on superheated compressed steam and compressed supercritical aqueous electrolyte solutions to the Isotope Development Center at the Oak Ridge National Laboratory where feasibility of the isotope separation process based on using high pressure supercritical steam as a solvent for ionizable salts is under consideration. In addition, if our small scale laboratory experiments dealing with separation of isotopes prove successful, we intend to develop a close working relationship with the Isotope Development Center at the Oak Ridge National Laboratory. If evaluation of the process at a practical scale is decided upon, we plan to assist with our expertise gained during our experiments.

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

At the University of Illinois our interaction with H. G. Drickamer, Professor of Chemical Engineering and Physical Chemistry, is very valuable for our work. We plan several direct collaborative projects in the near future. The success of our laser Raman scattering experiments can be related to our interaction with M. V. Klein, Professor of Physics, who is an expert in optical spectroscopy. Theoretical interpretation of our experimental results on order-disorder transitions and the hysteresis phenomena accompanying these transitions will require a collaborative effort with theorists in the Department of Physics. Our current and proposed studies of polymers do not represent an isolated effort at the University of Illinois because there are a number of researchers in the area of polymer engineering. A strong interaction with this group is anticipated.

Publications: (Calendar Year 1975)

J. Jonas, T. DeFries, and D. J. Wilbur
Molecular Motions in Compressed Liquid Water
J. Chem. Phys. (in press)
Also supported by ARPA DAMC 15-73-610 and AFOSR-75-3-0091

J. W. Linowski, Nan-I Liu and J. Jonas
The Effect of Density and Temperature on the Hydroxyl Proton Chemical Shift in Liquid Ethanol
J. Magnetic Resonance (in press)

M.S. Theses: (Calendar Year 1975)

None

Ph.D. Theses: (Calendar Year 1975)

None

Solid State Phase Transformations and Thin Films

Principal Investigator: C. Marvin Wayman, Ph.D.
Professor of Metallurgical Engineering

Supporting Agency: U. S. Energy Research and Development Administration

Senior Staff: C. Marvin Wayman, Professor
Kazuhiro Otsuka, Visiting Research Associate (Term 3/4/76)

Junior Staff: Michael P. Cassidy, Research Assistant
Atef H. Eltoukhy, Research Assistant
Jun Ichi Fujita, Research Assistant
Thomas E. Huson, Research Assistant
Myung-Hwan Kim, Research Assistant (Term 9/5/75)

Object: This work is centered around solid state phase transformations of the martensitic type and focusses on a number of interrelated phenomena. Studies of prenucleation and nucleation, mechanisms of growth, and properties of martensitically formed phases are of concern. Pretransformation phenomena, as recently found through work on this program, are being studied in further detail by electron diffraction and microscopy. We are attempting to understand apparent heterophase fluctuations which are revealed by diffuse electron scattering and "streaming" effects in electron microscope images. Related to this is a later stage of transformation where instabilities in the regions of lattice imperfections promote the first detectable signs of phase nucleation. Once nucleated, details of phase growth are determined with particular reference to the nature of the interface between the two phases, and considerable progress has been made in relating the observed dislocation structure of such interfaces to a probable growth mechanism, particularly in hydrides. The substructure of the final phases is studied in order to permit a comparison between it and properties of interest. For the most part, metallic hydrides and alloys exhibiting thermoelastic martensitic transformations are being observed. These are both of interest in the energy scene. Hydrides are potential materials for energy storage. Thermoelastic martensites usually exhibit the shape memory behavior and thus offer promise for the conversion of low grade heat (cooling wastes, solar) into mechanical energy. The emphasis is on fundamental research.

Results, FY 76:

Most Significant Accomplishments: Research on V_2H has shown that the formation of this hydride is very similar to that of conventional martensites. Electron microscopy has been employed to analyze the dislocations and their Burgers vectors situated in the hydride-matrix interface. From the Burgers vector and spacing of these dislocations, an inhomogeneous shear has been deduced, the magnitude of which is in remarkable agreement with the habit plane, orientation relationship and shape strain, assuming the transformation to occur martensitically. The mechanistics of this type of transformation are becoming quite clear, and it remains to extend the work to other systems for generalization.

Other Results: Studies on the mechanical behavior of Cu-Al-Ni martensites have shown a new mode of deformation. Whereas at low strains twin boundary motion within martensites occurs, and plates with preferred Schmid factors grow at the expense of others; at high strains a new transformation to a different martensitic structure occurs, i.e., a martensite-to-martensite transformation. This behavior is believed to be typical of a number of thermoelastic martensites, and is capable of producing quite large strains (i.e., 20%) which are fully recoverable when the applied stress is released. This new type of deformation behavior (from γ_1 to β_1 in Cu-Al-Ni alloys) has also been found in Cu-Zn alloys, in which case the crystal structure of the final phase is now under investigation.

Additional studies of Cu-Al-Ni and Cu-Zn martensites have shown that certain thermoelastic martensites form by a mechanism of internal faulting, the end result being a long period stacking structure of the 9R or 18R type. Analysis has shown, and a theoretical model has been presented, to explain how internally faulted martensites are capable of complete crystallographic reversibility, and to explain pseudoelastic and shape memory behavior. It was previously considered that such faulted martensitic phases resemble slipped crystals and cannot exhibit reversibility. However, the additional presence of crystallographic ordering presents strong restrictions on slip and faulting, and requires an inverse deformation which imparts the observed reversibility.

Continued studies of pretransformation lattice instabilities in several copper alloys by electron microscopy have demonstrated that a pronounced temperature effect exists. Diffuse electron scattering and image instability become more marked at lower temperatures. This is exactly as expected. However certain "electron stimulation" anomalies have been found even in dummy materials such as pure copper which do not undergo any phase transformation, and this observation is being pursued.

Studies of the thermodynamics of thermoelastic martensites have shown that in the first approximation "engine efficiencies" of the shape memory effect may be as high as 20%. This analysis depends on an accurate delineation of two "characteristic" temperatures associated with a thermoelastic martensitic transformation. The first of these is the T_0 , the temperature where the chemical free energies of the two phases are equal, and the other is a T_0' temperature, which is the former temperature, T_0 , modified by the presence of accumulated elastic energy. Theoretical work has continued to establish the fixing of these temperatures for a given transformation and to determining the magnitude of the stored elastic energy.

Results Expected, FY 77: This research will be supported by the National Science Foundation beginning July 1, 1976.

Relationship to Other Federally Funded Projects: Research on the formation of hydrides in metals has involved a study of the vanadium hydrogen system, and in the near future will be extended to the zirconium-hydrogen system. This work is in collaboration with Professor T. E. Scott of the Ames Laboratory and Professor J. S. Bowles of the University of New South Wales. Efforts at the University of Illinois are centered on electron microscopy and diffraction studies. The Ames group is concerned with hydrogen charging, and specimen preparation, analysis and characterization. The work at the University of New South Wales focuses on x-ray crystallography, metallography, and Kossel line techniques. Work on martensitic transformations is related to that sponsored by the National Science Foundation on Shape Memory Alloys. A part of the present research on pretransformation lattice instabilities is in collaboration with Professor S. C. Moss at the University of Houston. Whereas the Illinois efforts involve purely electron microscopy and diffraction techniques, parallel efforts on Cu alloys involving neutron diffraction measurements are being carried out by Professor Moss and the Brookhaven group during the summer months. Work here on thermoelastic martensites is related to the engineering and design research on Nitinol engines at the Lawrence Berkeley Laboratories. Cooperative aspects of the above programs will be continued. Information is exchanged weekly at a seminar devoted to martensitic transformations and related aspects, Met. E. 494.

Publications: (Calendar Year 1975)

T. P. Darby and C. M. Wayman

Growth of Gold Thin Film Dendrites on Graphite Substrates

J. Cryst. Growth 29, 98-108 (1975)

T. P. Darby and C. M. Wayman

Nucleation and Growth of Gold Films on Graphite I: Effects of Substrate Condition and Evaporation Rate

J. Cryst. Growth 28, 41-52 (1975)

K. Otsuka and C. M. Wayman

On the Shape Memory Effect in Internally Faulted Martensites

Scripta Met. 9, 1017-1022 (1975)

H. C. Tong and C. M. Wayman

Thermodynamic Considerations of 'Solid State Engines' Based on Thermoelastic Martensitic Transformations and the Shape Memory Effect

Metallurgical Transactions 6A, 29-32 (1975)

Also supported by NSF

H. C. Tong and C. M. Wayman
 Thermodynamics of Thermoelastic Martensitic Transformations
 Acta Metall. 23, 209-215 (1975)
 Also supported by ARO (Durham)

C. M. Wayman
 Deformation, Mechanisms and Other Characteristics of Shape Memory Alloys
Shape Memory Effects in Alloys, edited by J. Perkins (Plenum Pub. Co.,
 New York, 1975), pp. 1-28
 Also supported by ARO(D) and NSF

C. M. Wayman
 Shear Transformations and Microstructure
 Metallography 8, 105-130 (1975)
 Also supported by ARO (Durham)

C. M. Wayman and T. P. Darby
 Nucleation and Growth of Gold Films on Graphite II: The Effect of Substrate
 Temperature
 J. Cryst. Growth 28, 53-67 (1975)

K. Otsuka and C. M. Wayman
 Pseudoelasticity and Stress-Induced Martensitic Transformations
Reviews on the Deformation Behavior of Materials (accepted)

M.S. Thesis: (Calendar Year 1975)

H. Cassidy (C. M. Wayman, Adviser)
 An Electron Microscopy Study of the Substructure of β -Hydride in Vanadium
 May 1975

Ph.D. Thesis: (Calendar Year 1975)

S. Chakravorty (C. M. Wayman, Adviser)
 Crystallography of the Thermoelastic Martensitic Transformation in Ni-Al Alloys
 1975

Physics of Refractory Materials

Principal Investigator: Wendell S. Williams, Ph.D.
Professor of Physics, Ceramic Engineering,
and Bioengineering

Supporting Agency: U. S. Energy Research and Development Administration

Senior Staff: Wendell S. Williams, Professor
Dwight Jennison, Research Associate

Junior Staff: David L. Klein, Research Assistant
Marvin W. Johnson, Research Assistant
James R. Bethin, Research Assistant
Gerald H. Yost, Research Assistant
Barbara Browning, NIH Fellow
Roger Johnson, NIH Fellow

Object: The development of new energy technologies--coal gasification, MHD, fuel cells, breeder reactors, fusion, solar devices--will be limited by the performance of materials under conditions of extreme temperature, stress, radiation, corrosion and erosion. The scope of this project involves a wide-ranging scientific study of a specific class of ceramic materials possessing extreme values of hardness, melting point, abrasion resistance, superconducting transition temperatures and low chemical reactivity that might be matched to these extreme operating conditions.

When the research supported by this project was initiated several years ago in an industrial laboratory, there was modest interest in improved high-temperature materials in industry and considerable though transient interest in the defense agencies. With the advent of the energy crisis the need for such materials became more serious and again was focused in the civilian sector. During these years, a considerable body of fundamental knowledge about the ceramic materials under study has been developed. It is the goal of this subproject to extend, refine and direct this knowledge in the light of recently-perceived energy needs.

The ceramic materials receiving particular attention in this project are the monocarbides of the transition metals of columns IV, V and VI of the periodic table, Ti, Zr, Hf, V, Nb, Ta, and W. These are some of the so-called "refractory hard metals," a name that suggests at once a scientific puzzle: how can metallic conductivity and great hardness coexist in the same solid? The puzzle is further complicated by the characteristically ionic (NaCl) crystal structure of most of these materials. It appears that the transition-metal carbides exhibit features usually associated with each of the three principal types of bonding studied in solid state physics--metallic, covalent and ionic. A major objective during the study of these materials has been to determine whether the

features of electronic conductivity, great hardness and crystal habit are indeed characteristic of the materials or whether they are controlled by impurities or other defects. A conclusive answer to this question has been reached, though it includes an ironic twist. From calculations of the energy band structure, performed recently in this group, but agreeing qualitatively with most earlier calculations, it is clear that the transition metal carbides are semimetals. The density of states curves show no gap. When the vacancies are disordered, as is usually the case, they contribute heavily to the electron scattering; however, this research has also shown that the resistivity of the carbides can be completely controlled by the defect structure. These materials are non-stoichiometric, and the lack of stoichiometry is exhibited in the form of carbon atom vacancies. When the vacancies are ordered as in $V_6C...$, as we have shown, the resistivity drops. For special applications, for example as lead-ins for current in a corrosive environment or at high temperatures in a fusion reactor, a refractory hard metal might be very useful.

Vacancies scatter not only electrons but also phonons. This research effort has contributed to the analysis of the role of carbon vacancies in heat transport in the carbides, finding that at low temperatures the vacancy scattering is far less important than that due to phonons interacting with conduction electrons. At high temperatures, however, the vacancy scattering is significant and can alter the thermal conductivity over a considerable range both from reduction of electron-vacancy scattering and from phonon-vacancy scattering. The increase in thermal conductivity due to electronic component in these metallic materials is one of the reasons for the renewed interest in the advanced nuclear fuel, uranium carbide, a solid quite similar in physical properties and structure to the transition-metal carbides. With a wide range of vacancy population available without change in crystal structure, the carbides offer a design engineer a large range of values of conductivity for optimization.

In addition to transport of electrons and phonons in the carbides, this project has studied atom transport; in particular, the electromigration and chemical diffusion of carbon in nonstoichiometric titanium carbide. Because of the high vacancy concentration, the activation energy for diffusion of carbon represents exclusively the migration term, though this term is large (4.5 eV) due to the strong covalent bonding.

Plastic deformation and dislocation behavior in the carbides have also been given considerable attention in this project and will again become prominent as more structural applications are envisioned in energy technologies. During FY 76 a new effort was started on the influence of electric fields and adsorbed molecules on the measured surface hardness of ceramic materials. Various interesting but ill-understood results have been reported in the literature indicating that an applied electric field produces a reduction in hardness of semiconductors. We will duplicate the measurements and, if the results are confirmed, attempt to provide an interpretation. The phenomenon is at the heart of the relationship between electronic structure and dislocation properties that has motivated two of our recent Ph.D. thesis projects. Clarification of

these matters would go far to explain micro plastic deformation of hard materials in temperature regions where dislocation glide does not readily occur. Improved understanding of this matter might suggest ways of reducing the brittleness of these and other refractory materials and thereby increase their utility for applications where light weight and high strength are required, as in energy-saving vehicles and wind conversion.

The second new project launched during FY 76 is in a heavily-worked but ill understood area, catalysis. Since tungsten carbide, one of the carbide family under study here, is the second best catalyst known after platinum for oxidation of hydrogen in the fuel cell by electrocatalysis, we have decided to apply the detailed knowledge of the material developed here to this, for us, new area to see if general ideas or principles of catalysis can thereby be isolated or tested. For example, there is reported to be a strong correlation between defect concentration (carbon vacancies) in WC and its catalytic activity. We intend to study this relation in more detail and test the hypothesis that point defects are the sites of catalytic activity on a surface. Another hypothesis to examine is provided by the theoretical work of A. B. Kunz and others in the MRL: a metal catalyst must have a $4s^2$ electronic configuration at the surface. We will study the difference in catalytic effectiveness of TiC and WC with reference to both these ideas--the necessity for vacancies and^x for a specific electronic structure.

Inasmuch as the behavior of ceramic materials is the unifying theme of this program, we have extended the study to include biological ceramics, especially teeth and bone.

The program of research carried on and projected for this program, though centered on materials rather than techniques, has developed expertise and equipment for mechanical testing in vacuum at high temperatures, X-ray topographic studies of dislocations, and high-impedance electrical measurements. Apparatus to be acquired during FY 76 will allow measurements of electrocatalytic activity and microhardness. In addition to these techniques, the project makes extensive use of the central facilities of the MRL, especially the electron microscopes and the computer.

Results, FY 76:

Most Significant Accomplishments: The most significant result obtained during FY 76 was the refinement of our understanding of the origin of strong bonding in the refractory carbides, through the application of local orbitals techniques for solving the Hartree-Fock equation for solids. This work was conducted by a research associate (D. Jennison) who learned the computational techniques from Professor A. B. Kunz of the Illinois MRL. Since a major potential use for these ceramic materials is in structural parts for high-temperature applications (e.g., in turbines), a better fundamental understanding of the relation between the electronic

structure of the solid and its mechanical properties is required for optimizing the performance.

The calculations show that there is strong covalent interaction between the carbon 2p states and the metal 3d and 2s states. The resulting orbitals are directed and rigid, thus accounting qualitatively for the hard and brittle character of the materials. A small Madelung contribution to the energy is also found. The calculations done by this method are the most rigorous and accurate yet attempted for this class of solids with mixed binding character.

The electron energy bands have also been calculated for TiC with the local orbitals approach. Whereas the general shape of the bands is in agreement with other calculations using APW methods, the importance of the present result is that it is self-consistent and has no adjustable parameters or empirical input. Thus this band structure should be a definitive one for the material studied.

Other Results: A related result from this effort, which is closely tied with Professor Kunz's group, is an approximate treatment of clusters of atoms using a computational scheme which is much faster than the unrestricted Hartree-Fock method. The cluster program is now essentially in finished form, and with it studies can be made of defects and surfaces of these solids (see FY 77).

Another result obtained during FY 76 is an interpretation of the temperature dependence of the residual resistivity of the nonstoichiometric carbides. In these solids, as we have demonstrated (Ph.D. thesis by L. Shacklette, 1970), the carbon vacancies act as strong scattering centers for conduction electrons. Since the crystals are nonstoichiometric, there is a large vacancy population to provide the scattering centers. Low temperature resistivity measurements show an exceptionally large residual resistivity, but this quantity is strongly temperature-dependent, in disagreement with the simple form of Matthiessen's rule. Although the residual resistivity accounts for approximately 50 micro-ohm cm at liquid helium temperature, it only contributes approximately one-tenth of that at 1000°C. A curve of residual resistivity versus temperature for vanadium carbide was obtained previously by subtracting the measured resistivity for an ordered vanadium carbide (V_6C_5) from that for a disordered sample ($VC_{0.84}$). We have now shown that the functional dependence of the residual resistivity on temperature can be fitted exactly by a model based on the temperature dependence of the Fermi energy for a solid with slightly overlapping energy bands. This situation obtains for TiC and VC, where the Fermi energy falls near the minimum between a filled bonding band and an unfilled antibonding band derived from metal 3d and carbon 2p states. This result and others characterizing electron scattering by defects in the carbides will be presented at an invitational conference on solid compounds of the transition elements in Uppsala, Sweden, in June, 1976.

Another clarifying interpretation of the peculiar behavior of the carbides was provided by work during FY 76: the increase in the electronic contribution to the thermal conductivity of TiC at high temperatures reported in the literature was analyzed in terms of bipolar diffusion of electron-hole pairs diffusing down the temperature gradient and recombining with release of energy--i.e., transport of heat. This process is well known in semiconductors, and following the suggestion of Gallo, et al., for semi-metals, we have applied the calculation to the carbides. Since the experimental data available show considerable dispersion, it is difficult to demonstrate that any specific mechanism is active in this high-temperature transport process, but the results obtained here indicate that the bipolar diffusion interpretation could be and probably is correct.

Last year, we looked ahead to trying to apply the model of electronic damping of dislocation kink motion in covalent solids developed here (Ph.D. thesis, A. P. Gerk, 1973) to our recent measurements of dislocation velocities in Si (Ph.D. thesis, S. Kulkarni, 1975). This analysis was completed during FY 76 and showed, as hoped, that the motion of individual dislocations over macroscopic distances in pure and doped Si can also be interpreted by the electronic damping theory. As the kink moves at the high temperatures required, the local equilibrium of electrons and holes in the conduction and valence bands is disturbed; relaxation to the equilibrium state is facilitated by internal Auger recombination processes. The probability for these processes increases as the concentration of electrons or holes in the bands. Thus a doped sample will come back to equilibrium faster than an undoped one as a kink moves in the solid, so the effective force opposing kink motion will diminish. One should see a reduction in the activation energy for motion of dislocations. The experimental results bear out this prediction: the activation energies for dislocation motion in both n and p type Si are reduced by a factor of one-half the band gap over that found for pure Si, in accordance with the prediction of the model. Thus two experiments in this group--internal friction in Si and dislocation velocity measurements--support the idea that electronic drag effects limit dislocation motion in covalent solids at high temperatures. If this result stands, it will be an important contribution to our understanding of how hard, brittle materials soften at high temperatures. Such understanding is important in the selection and design of materials for use in any high-temperature system where retention of high-temperature strength is important (e.g., fusion reactor, advanced nuclear reactors, MHD generator, etc.)

An important result was obtained in FY 76 on another hard, brittle material--bone. Our previous work on the electrical properties of this material demonstrated that the signals produced in bending beams cut from long bones could not be analyzed in terms of the usual third-rank tensor theory of piezoelectricity but instead required a fourth-rank tensor formalism. Other bone research groups have raised questions about the ultimate biological importance of this finding since the measurements were made

on dried specimens. During the last several months we have repeated the measurements of bending "piezoelectricity" on moist bone specimens, including some that were freshly excised. In all cases, the qualitative features that demonstrated the need for a fourth-rank tensor theory for dried bone were duplicated with the moist specimens. We conclude that the findings may indeed be important for biology. With colleagues from Veterinary Medicine we have demonstrated the necessity for electrical signals in the normal functioning of growing bone by inducing osteoporosis in immobilized rabbit bone and preventing it in other immobilized rabbits by supplying the missing electrical signals artificially through implanted electrodes.

During FY 76 the principal investigator returned to the Laboratory from a one-year leave of absence as an Energy Research Coordinator for the National Science Foundation, Washington, D. C.

Results Expected, FY 77: During FY 77 we expect substantial progress on a new project, the role of lattice defects in catalysis. An experimental program is being initiated in FY 76 for a study of the influence of deviations from stoichiometry on the electrocatalytic activity of tungsten carbide in the oxidation of hydrogen in a fuel cell. By the end of FY 77 this project should have added to the experimental data already in the literature which indicate increasing activity with increasing deviation from stoichiometry (increasing concentration of carbon vacancies). In addition, the project should produce better characterization of the nature and magnitude of this deviation. Comparative results on WC_x and TiC_x should further define not only the dependence of catalytic activity on carbon vacancy concentration, $1-x$, but also on the symmetry of bonding orbitals in the neighborhood of the point defect, since TiC is cubic and WC is hexagonal. In addition, some conclusions about the role of an oxygen atom substituted for carbon in the vacancy should be available. We expect experimental results on powders of the carbides and on single crystals, in two quite different experimental geometries. In both cases, the results will be used to test predictions made from the concurrent theoretical effort, which uses cluster methods to calculate the binding energy of hydrogen to specific surfaces, with and without defects, including vacancies and substitutional impurities. The principal result anticipated from this research project during FY 77 will be strong evidence either supporting or contradicting our present hypothesis that the active site for catalysis on solid surfaces is a point defect.

By the end of FY 77 an investigation of the reported relation between zeta potential, applied electric field and surface hardness of ceramics should have been brought to the point of confirming or contradicting the claims in the literature. If the claims are borne out, the application of different models to interpret the results will also be well along by the end of this period.

The local orbitals calculations of total energy of all the carbides should be completed by the end of FY 77 and from these results the planned calculation of elastic constants should also be completed. Detailed comparison with experimental values where available should by this time allow one to assess the utility and accuracy of the theoretical methods in predicting certain mechanical properties of the solid from detailed knowledge of its electronic structure. The calculation of electron densities in real space should also be completed during this period.

In addition to the results expected in FY 77 on synthetic ceramic materials, a conclusion should be reached concerning the origin of electrical effects in the biological ceramic, bone. Experiments planned for the coming year will either support or refute the Japanese proposal that the bending "piezoelectricity" observed in bone results from displacement of excess space charge. Electrical properties of selected polymers subjected to electron irradiation and charge injection by high dc fields will be compared against the predictions of the Japanese theory.

Results Expected, FY 78: Additional evidence on the suspected relation between point defects and catalysis will be accumulated during this period if the relation is substantiated by the results of FY 77. This theme is of such general significance to the basic science underlying an important energy-saving mechanism that the work will be continued for several years and expanded, providing that it is on the right track. The experimental studies planned for the carbides in the area of catalysis will be extended during this period to oxides. The theoretical results coming from A. B. Kunz's group suggest that the oxygen atom is an important component of some catalytic processes. Since metal surfaces are generally covered with an oxide film in practical situations, even metal catalysts may operate through the mediation of an oxide or at least a cluster of oxygen atoms. This possibility will have been explored for the specific case of oxygen substituting for carbon in the nonstoichiometric carbides in FY 77; in FY 78 the study will be extended.

The data accumulated on surface environment and hardness of semiconductors, insulators and semimetals during FY 77 will be analyzed during FY 78 and specific models explored. The tunneling hypothesis advanced by Gilman, for example, should either be supported or rejected by the analysis. The models of electron interactions with moving dislocation kinks developed by Gerk and furthered by Kulkarni in this group may have a bearing on the surface hardness problem and will be examined for this purpose.

The cluster calculations begun in FY 76, and applied to defects at the surface of carbides in relation to catalysis in FY 77 will be carried further in FY 78 in collaboration with Kunz's group. The local electronic environment near a vacancy in the bulk will be treated in detail to calculate vacancy interaction energies which lead to the ordering of some

of the nonstoichiometric carbides. These ordered compounds, V_6C_5 and V_8C_7 , for example, have already been studied to show the dramatic reduction in residual electrical resistivity accompanying the ordering, but no understanding presently exists of why the ordered phases represent a lowering of the total free energy. To exploit the improvement in properties in the ordered phases for applications to energy technologies where better refractory materials of high electrical conductivity are needed, we need also to understand the reasons for the ordering so that ordered phases can be custom-designed.

Other important results from the theory effort, continued in collaboration with A. B. Kunz, should be forthcoming as the general scheme of predicting mechanical properties from the electronic structure is developed. The temperature-dependence of the hardness, discussed above as a limiting practical characteristic of the refractory carbides, will be examined during FY 78 to see how much of the effect is due to spatial delocalization of bonding orbitals resulting from thermal fluctuations. This line of approach would be separable from studies of dislocation glide and climb, and the diffusion of carbon and/or metal as mechanisms responsible for plastic deformation. Some information is available on these processes, and will be reviewed and extended as necessary, such that by the end of FY 78, a reasonably complete picture of the temperature-dependence of the hardness of the carbides can be given. With this detailed knowledge, strategies can be devised to reduce the amount of plastic deformation in these ceramic materials at high temperatures through alloying, doping, etc.

An effort that would complement the study of high temperature softening in the carbides is a study of the room-temperature brittleness. This characteristic is also very limiting to the utilization of these materials. With the knowledge being developed from the theory program on electron distribution in the materials, and on the location and strengths of the various covalent bonds, it should be possible to recommend doping and alloying agents that would reduce the bond energy and hence also reduce the Peierls stress controlling dislocation kink formation. These two complementary studies will be conducted in FY 78 if possible and might lead to suggestions for designing improved modifications of critically-needed structural ceramics for future energy technologies.

Relationship to Other Federally Funded Projects: The single crystals of the transition-metal carbides that have been obtained through the years by purchase or gift are shared with other investigators in the Illinois MRL. For example, Professor Klein's group has studied Raman scattering in crystals of titanium carbide and has found, as expected, that the defect structure of these nonstoichiometric solids allows Raman scattering events to occur even though the crystal structure is cubic. These results are being compared with similar activity at Oak Ridge. The measurements are among the first on metallic systems and should in time help in a more detailed characterization of the electronic structure in the neighborhood of the carbon vacancy--the defect in this class of materials that controls all the transport properties.

Discussions with Professor F. Brown in the Illinois MRL have led to a plan for study of the X-ray absorption edge as a function of carbon/metal ratio in the transition-metal carbides. Again, the crystals on hand will be used. Although similar measurements have been conducted at Wright Field and at Uppsala, the combination of local expertise in these materials and in the X-ray measurements should produce definitive results that can be incorporated in a more comprehensive view of the behavior of the carbides.

The recent extension of the present program of research to a study of catalysis in tungsten carbide has made contact with the theoretical studies of catalysis under Professor Kunz of the Illinois MRL. Preliminary results from his theoretical methods have been obtained, at our suggestion, on the possible reasons for the gross difference in catalytic activity for WC compared with TiC.

Another research effort in the Illinois MRL on transition metal carbides--specifically the cemented carbides used for machining purposes--has recently been initiated through the Department of Ceramic Engineering with NSF funding. This effort is obviously closely related to that supported under the ERDA block grant through this project but is distinguishable through the specific nature of the purpose for which the NSF grant was made: to test the proposition that the primary cause of early failure of cemented carbide cutting tools is the rapid softening of carbides at high temperatures. Preliminary results on this subject were obtained under ERDA support in FY 75 (Baldoni).

Collaborative work with Oak Ridge on graphite for orthopedic implants continues but at a reduced level, as the nearby facilities at the University of Tennessee are utilized more extensively by Oak Ridge.

A natural interaction with the investigators in the Illinois MRL working on interstitials in transition metals will be developed in the coming year. The materials studied, the transition-metal carbides, are sometimes called "interstitial compounds" and represent a limiting case of the introduction of interstitial carbon into a matrix of a transition metal.

The recent activity of this group (two Ph.D. theses) in the area of dislocation motion in covalent solids, including one study of internal friction, provides a potential link with other strong efforts on dislocation behavior in solids pursued in the Illinois MRL by several other investigators, including Professors Granato, Koehler and Birnbaum. This potential will be explored in the coming year.

For several years, this group has carried on a project to analyze and interpret the piezoelectric behavior of natural bone. Additional support for this project has now been obtained from another federal agency, NIH, which is carrying one graduate student in physics as a Trainee in the Bioengineering Program Traineeship Grant on the Urbana campus.

Publications: (Calendar Year 1975)

Lance Breger, Marvin Johnson, and Wendell Williams
 Piezoelectric Response of Inorganic and Biological Materials Subjected to
 Inhomogeneous Stress
 J. App. Phys. (submitted to)

Dwight R. Jennison and A. Barry Kunz
 Degree of Ionicity in Crystalline NaF, NaCl, SrF_2 and SrCl_2 as Found by Local
 Orbitals Hartree-Fock
 Phys. Rev. (submitted to)
 Also supported by NSF-DMR 72-03026 and ARL F33615-72-C-1506

S. B. Kulkarni and W. S. Williams
 Dislocation Velocities and Electronic Doping in Silicon
 J. Appl. Phys. (submitted to)

M.S. Theses: (Calendar Year 1975)

None

Ph.D. Theses: (Calendar Year 1975)

Joseph Gary Baldoni II (W. S. Williams, Adviser)
 High Temperature Deformation Behavior of Cemented Carbide Cutting Tools
 January 1975

Subhash B. Kulkarni (W. S. Williams, Adviser)
 Velocities of Screw and 60° -Dislocations in Intrinsic and Extrinsic Silicon
 October 1975

ED-02-01-02-0 Mechanical PropertiesInterstitial Solid Solutions

Principal Investigator: Carl J. Altstetter, Sc.D.
Professor of Physical Metallurgy

Supporting Agency: U. S. Energy Research and Development Administration

Senior Staff: Carl J. Altstetter, Professor

Junior Staff: Gary L. Steckel, Research Assistant
Peter F. Tortorelli, Research Assistant

Object: The objective of this program is to discover and understand the behavior of group V refractory metals, vanadium, niobium and tantalum, and to assess some aspects of their suitability for energy-related applications. Of particular concern in potential nuclear applications are the reactivity and degradation of these metals by oxygen in their operating environments. One part of the program deals with the solubility of oxygen and the compositional dependence of the enthalpy and entropy changes when oxygen dissolves in the metals. These quantities are used to test statistical mechanical interstitial solution models and to infer atomic interaction parameters. It is expected that this will significantly improve our understanding of the energetics of interstitial solid solutions of bcc metals. The principal technique is the measurement of the equilibrium potential developed in solid state galvanic cells having different metal oxygen alloys as electrodes and an oxygen ion conducting electrolyte. Measurements are made in the range 650°C to 1250°C--just the temperature range these metals would experience in nuclear structural applications.

The other part of the program is a study of the effects of energetic ion bombardment on the sputtering of metal atoms and the resulting surface topography. This problem is relevant to the use of materials in fusion reactors where structural integrity and high vacuum compatibility of the material is important. Of even greater importance is contamination of the plasma with metal and adsorbed and dissolved atoms, leading to greater plasma energy losses and inability to achieve critical confinement at sufficiently high temperatures. Niobium and vanadium and their alloys with oxygen are exposed to H^+ , He^+ and A^+ ion beams at up to 30 keV energy. Our scientific objective in this part is to test sputtering theories and determine the processes by which topographical features form and evolve. Sputtering yield is measured by optical and weight loss measurements. Scanning electron microscopy, interferometry and microprofilometry are used to assess the topographical changes. Auger electron and x-ray spectrometry are used to determine surface compositional changes and electron channeling is used to determine structural damage and crystallographic information.

Results, FY 76:

Most Significant Accomplishments: Determination of the solubility and the chemical potential of oxygen in vanadium. Identification, for the first time, of a cyclic atom removal process during sputtering.

Published work by N. Carlson of Ames Laboratory and D. Smith of Argonne Laboratory were in sharp disagreement on the solubility of oxygen in vanadium, differing by about a factor of two. Using our emf technique we were able to verify the results of one of the groups. We are presently exploring with the other group the reasons for our disagreement. Besides the basic scientific interest, our results on this system are important to one of the techniques for monitoring the oxygen content of the sodium coolant in the LMFBR program. We were able to formulate analytical expressions which describe the activity of oxygen in vanadium for all compositions in the single phase region in the temperature range from 650°C to 1250°C. Below 3.0 at.% O the solutions obey Henry's law, but deviate significantly above that composition. A correlation using Darken's alpha parameter proved successful at higher compositions.

Production of V-Nb-O alloys has begun for the next phase of this work.

In FY 76 our ion beam apparatus became operational. Our early experiments using 15 keV argon ions on Nb and Nb-O alloys underscored the need to consider the orientation dependence of sputtering yield in polycrystalline specimens, particularly when dealing with materials having a crystallographic texture. Differential sputtering of grains can give rise to a stepped structure and ultimately to cyclic rather than steady state surface irregularity. We suggest a ledge mechanism to account for the cyclic production and destruction of surface irregularities. There is evidence suggesting that these surface irregularities--cones--are intrinsic features rather than due to impurity solutes or phases. The significance of these results is that the rate at which material is lost from the first wall of a fusion reactor may be greater than that predicted by measurements on single crystals. Of further significance is the implication that techniques which depend on sputtering for surface chemical analysis (Auger spectroscopic profiling, secondary ion mass spectroscopy) may have less depth resolution than generally assumed, due to differential sputtering and cone formation. Apparatus for in situ sputtering yield measurement is under construction. Sample holders for elevated temperature and for simultaneous stressing, heating and irradiating are being designed.

Results Expected, FY 77: In the research with oxygen in solution we hope to complete the work with V-Nb-O alloys. This particular ternary system is chosen because we already have determined the complete thermodynamic description of both binary systems. (The Nb-rich and V-rich alloys allow us the opportunity of measuring solute-oxygen interactions in which the solute has a higher or a lower affinity for oxygen, respectively. The results will be used in several of the statistical formulations for interstitial solid solutions to test their validity and to predict ternary behavior from a knowledge of binary system behavior. If possible, measurements on the V-Mo-O or Nb-Mo-O systems may be used to predict Mo-O binary system behavior.

If a modest increase in manpower is available, it will permit an immediate expansion into the use of thin layer galvanic cells in which the electrodes and electrolyte are deposited from the vapor phase. This would give a

tremendous boost to the application of the emf technique to much lower temperatures or to faster response at high temperatures. Such thin film devices could prove useful for on-line control of combustion processes for more efficient utilization of fuels. They may also open up the field of cathodic protection of refractory metals against mildly oxidizing environments. Another possibility would be batteries or fuel cells for elevated temperature operation.

In the sputtering work we expect to have results on creep enhancement under ion irradiation conditions. We also will be making yield measurements on other materials besides Nb, V and their alloys. FY 77 should see results using targets of low Z materials such as aluminum, sintered aluminum powder (SAP) and aluminum/graphite or aluminum/SiC composites. Experiments will also be done using lighter ions, H^+ and He^+ . The effort in this part of the program will be to minimize target erosion and plasma contamination by manipulating the metallurgical structure of the material. Experiments on neutron irradiated materials will continue.

Results Expected, FY 78: The oxygen work could branch into another or into two related projects, depending on the results in FY 77 and the level of support. One of the projects would be a continuation of the fundamental work on alloys containing oxygen and the development of solid solution models. The other branch would concentrate on thin film galvanic cells, described briefly under FY 77 expected results. The former option would probably be followed if no increase in support level is forthcoming. In the sputtering work we will continue using different target materials, trying to strengthen our knowledge of sputtering mechanisms and demonstrate generality of our observations. Surface coatings and compositional modification of surfaces will be investigated. More effort will be expended in transmission electron microscopy to assess the near-surface damage due to ion bombardment. Collaboration will be sought for 14 MeV neutron-damaged specimens and/or high energy heavy metal ion irradiation prior or subsequent to ion damage. It is hoped that Rutherford back-scattering capabilities will be available on campus as an analytical tool in this time period. Such measurements would greatly enhance our ability to characterize coating and compositional alterations.

Relationship to Other Federally Funded Projects: Close cooperation is maintained with the MRL project of R. Yeeke, with whom we share equipment for the annealing and oxygen doping of refractory metal specimens. Likewise, with C. Wert's MRL project we share use of the zone melting apparatus for the production of binary alloys of refractory metals. There is also a close relationship with H. Birnbaum's MRL group which has supplied us with ultra pure test material. With all these groups there is more than just equipment sharing, because we freely exchange information on alloying behavior, heat treatment and handling techniques peculiar to the refractory metals with which we all work. The coordination is such that between us we study all the interstitial solutes--C, O, N and H--in niobium and vanadium, but do not duplicate any of our efforts. The potential for

duplication of effort is greater with groups working on oxygen in vanadium at Ames Laboratory and Argonne National Laboratory. Unwarranted overlap has been avoided by maintaining frequent communication with workers at these laboratories. In our sputtering work we are beginning joint experiments with M. Wechsler of Ames Laboratory to determine yields in neutron damaged vanadium oxygen alloys. This allows us to come one step closer to fusion reactor conditions.

Publications: (Calendar Year 1975)

None

M.S. Theses: (Calendar Year 1975)

None

Ph.D. Theses: (Calendar Year 1975)

D. Shah (C. J. Altstetter, Adviser)
Deformation of Vanadium Containing Dispersed $V_{16}N$ Particles
October 1975

Hydrogen Behavior in BCC Metals

Principal Investigator: Howard K. Birnbaum, Ph.D.
Professor of Physical Metallurgy

Supporting Agency: U. S. Energy Research and Development Administration

Senior Staff: Howard K. Birnbaum, Professor
Chee Gregory Chen, Research Associate
Muneyuki Amano, Visiting Research Associate Professor

Junior Staff: Joseph J. Au, Research Assistant
Gerald R. Matusiewicz, Research Assistant
Robert Sherman, Graduate Student
Philip E. Zapp, Research Assistant

Object: The primary focus of this work is on the behavior of light interstitial elements in metals. In the past few years and during the next contract period, emphasis has been and will be on the refractory metals Nb, Ta, and V, on the ferrous alloy systems, and on the interstitials hydrogen, deuterium and helium. Four aspects of the behavior of these systems are being investigated; (a) the diffusion of the interstitial solutes, (b) the local vibrational modes of the interstitials (with M. Klein), (c) the precipitation of hydrides (with H. L. Fraser), and (d) the behavior of H(D) and H₂S on the surfaces of the refractory metals (with M. Klein).

The behavior of light interstitial elements in bcc metals is of major scientific interest as they represent systems in which the diffusion occurs by a quantum mechanical tunneling mechanism. This behavior manifests itself by a marked deviation from the usual Arrhenius dependence of the interstitial jump frequency at low temperatures, by anomalously large isotope effects, and by extremely high diffusivities. These effects are being studied in the Fe-H(D) system using magnetic relaxation methods and in the Nb-H(D) system using the techniques of anelastic relaxation, anelastic piezoresistance, and the Gorsky effect. Since tunneling of the light interstitials is closely coupled to the lattice phonons, the local vibrational modes of H(D) are being studied in Nb, Ta and V using the methods of Raman spectroscopy.

Very little is known about the behavior of He in metals and essentially nothing is known about its behavior when present as an untrapped interstitial solute. This problem is being investigated using the above techniques in the Nb-He system. Since very appreciable concentrations of He are generated in components of the fission reactors and even greater quantities will form in the fusion reactor, this study has particular relevance to the problems of helium embrittlement and helium bubble formation.

In addition to the scientific interest in the behavior of the light interstitial elements, the above systems are of great technological significance in connection with materials behavior in energy production and transport. The problem of hydrogen embrittlement of technological alloys is present in both fission and fusion reactor systems as well as in coal gasification systems (where it is particularly aggravated by the presence of H_2S). In energy transport systems based on pipeline transmission of gases containing H_2 or H_2S the embrittlement by hydrogen is an increasingly significant problem. Additionally, the stress corrosion of many alloy systems appears to be intimately related to hydrogen embrittlement by gases released at the crack tip. As our previous studies have shown, the embrittlement of alloys by internal hydrogen is controlled by the kinetics of diffusion to a crack tip; hence we are studying the effects of H trapping centers such as O in Nb and C, N, and Ti in Fe on the diffusivity of H. Hydrogen embrittlement from a gaseous environment is controlled in part by the entry of hydrogen from the gas phase and we are therefore studying the behavior of H and H_2S on the surface of metals using the Raman technique. Embrittlement of the Group Vb elements is related to the formation and cracking of hydrides. The hydride precipitation mechanisms are being studied in these systems using transmission electron microscopy as a primary tool. In addition to the problem of hydrogen embrittlement, the hydride properties are of interest in relation to energy storage and transport. Energy storage in the form of hydrides is of particular interest in connection with "peak shaving" of power plants. Hydrides are also of increasing interest in connection with systems for refrigeration and mobile power generation.

The primary tool for the study of hydrogen mobility in Nb has been anelastic methods in the frequency range of 0.01 Hz to 300 MHz and in the temperature range 4 K to 300 K. The tunneling motion of H in the M-H and O-H pairs is being studied. In this low temperature range, single H solutes are present at concentrations below the sensitivity of the acoustic methods. The mobility of single H interstitials and the effects of O on this mobility is being examined using the Gorsky method which allows long range diffusion to be studied. The Gorsky technique is also being used at high temperatures to obtain reliable H and D diffusivities as these are of particular interest in the fusion reactor program. The anelastic methods also provide a means of studying the effects of trapping sites on hydride precipitation and information of this type is being gathered.

Application of the anelastic methods at low temperatures is somewhat limited by the low H and He concentrations which can be kept in solution. The anelastic piezoresistance technique is being developed to alleviate this constraint. In this method an acoustic wave is used to cause stress induced reorientation of interstitial solutes and ac resistance methods are used to study anisotropy of the electron scattering from these interstitials. This method is being applied to study the behavior of H in Nb at very low temperatures and of He interstitials in Nb.

The behavior of He in Nb is being examined in the temperature range of 4 K to 300 K. The He is being introduced in the interstitial form by ^3H decay to ^3He at 4 K and its behavior is being monitored at 4 K and during isochronal anneals with resistivity methods. A specific relaxation caused by stress-induced reorientation of the He is being sought using the piezoresistance method.

In the Fe-H system studies of H behavior require greater sensitivity than can be provided by the anelastic techniques due to the low H solubility. We will continue to use the magnetic relaxation techniques which we have developed and will apply them to a study of H trapping at interstitial and substitutional solutes. These effects are intimately related to the problem of hydrogen embrittlement of steels.

The Raman studies of H in Nb, Ta and V as well as on the surface of these elements will be continued and the studies of H_2S on the surface will be started. The problems of obtaining and maintaining a clean surface appear to be solved by carrying out the entire experiment in UHV and by cleaning the surface by electron beam heating. Our preliminary measurements indicate that the sensitivity is sufficient to examine both H(D) in solid solution as well as to see adsorbed species at the surface. The data is expected to yield information about the vibrational modes of H(D) in the interior and at the surface, the high temperature diffusivity of H(D), and density fluctuations of H at the spinodal critical point. Of particular interest will be studies of the effect of adsorbed species such as H_2S on the entry of H from the gas phase. This information is of great significance in understanding the embrittlement of materials by environments containing H_2S .

Results, FY76:

Most Significant Accomplishments: The quantum tunneling model for light interstitial solute elements in bcc crystals, which was proposed by Flynn and Stoneham, was shown to be correct for the motion of H in the OH complex in Nb. This is the first direct experimental confirmation of quantum tunneling of H. Measurements of the H jump frequency from about 300 K to 20 K (300 MHz to 0.01 Hz) were shown to fit the Flynn-Stoneham theory extremely well.

A theoretical model of H(D) behavior in bcc metals which is based on a delocalized H(D) interstitial has been developed in conjunction with C. P. Flynn of the MRL. This theory can account for a wide range of hitherto disparate and seemingly conflicting experimental results; the low temperature jump frequency and heat capacity measurements, the anomalous neutron diffraction Debye Waller factors, the diffuse X-ray measurements of distortion around the H(D) solutes, and the lack of anelastic Snoeck relaxations due to H(D).

Other Results: Analysis of the magnetic relaxation data for the Fe-H(D) system has shown that H(D) occupies three interstitial sites in the Fe lattice which are the octahedral, tetrahedral and triangular sites. These correspond to specific relaxation parameters which have been measured. It has also been shown that H(D) is very strongly trapped by C and N interstitial solutes with binding enthalpies of the order of 0.5 eV.

The crystallography of the OH defect in Nb has been established using anelastic techniques. It was shown that three types of OH clusters exist, a $\langle 100 \rangle$ nearest neighbor, $\langle 110 \rangle$ second nearest neighbor, and $\langle 111 \rangle$ third nearest neighbor pairs. The binding and reorientation enthalpies of each type of OH cluster has been determined.

The hydrogen isotope effects in both Nb and Fe have been established and are much larger than expected on a classical model. These effects may be consistent with a tunneling model, but at the present time are not accounted for by existing theories.

The Raman studies have demonstrated a surprisingly large sensitivity to H in the lattice and to H containing molecules adsorbed at the surface of Nb. These results suggest that the Raman technique will be extremely powerful in studying the vibrational and local phonon modes at surfaces and at H(D) solutes.

Results Expected, FY77: The program of studying the basic diffusion mechanisms of the light interstitial solutes in bcc metals will be continued. The anelastic piezoresistance method will be developed as a technique for studying the jump frequencies of interstitial solutes and clusters at extremely low concentrations. This technique will be applied to the H(D) behavior in Nb at very low temperatures in an attempt to observe the relaxations associated with single H solutes. Two types of relaxations will be examined (a) "diffusional" jumps of H(D) centered around nearest neighbor octahedral sites and (b) relaxations which result from a stress-induced change in the wave function of the delocalized H(D) solute. A parallel series of experiments will be carried out on the OH relaxations to extend the temperature range in which these are observed down to 4 K as a further test of the tunneling model for H(D) diffusion. It will be particularly interesting to examine the isotope effects at these very low temperatures.

The high temperature Gorsky effect measurements of H(D) diffusion in Nb should be completed during this contract period. These measurements will provide reliable high temperature data and should elucidate the effects of trapping on high temperature diffusion. The Flynn-Stoneham tunneling model of diffusion suggests that a negative curvature in the Arrhenius plot of the diffusivity should be observed at about 500°C. The experimental data should produce evidence for this effect if it occurs and will provide a further test of the tunneling model.

Use of Raman spectroscopy to study H(D) behavior in Nb, Ta and V will be continued. The main thrust of these measurements will be directed toward the behavior of interstitial H(D). As the experiments proceed, however, we will also be examining the vibrational modes which characterize adsorbed molecular species on the clean metal surfaces. Of particular interest will be the behavior of H₂S because of its significance in hydrogen embrittlement processes.

Helium diffusion studies in Nb will concentrate on establishing the behavior of interstitial He introduced by tritium decay. The primary measuring techniques will be resistivity measurements to establish the annealing behavior during isochronal anneals from 4 K and anelastic piezoresistance measurements to establish the relaxation behavior of the various forms of He. Particular attention will be focused on the effects of trapping sites on the diffusion.

The magnetic relaxation studies of H in Fe will be completed during this next contract period. The experimental work will determine the effects of substitutional solutes on the H(D) diffusion. These results will be of specific interest in understanding hydrogen embrittlement of steels.

Results Expected, FY78: It is anticipated that the program will evolve in a natural way from the results obtained in FY 77. The magnetic relaxation experiments on the Fe-H(D) system described above should be completed and at present it is not anticipated that this line of research will be continued. It is also anticipated that the characterization of the OH defect in Nb will be completed. The focus of the anelastic and anelastic piezoresistance experiments will be on determining the behavior of single H interstitials in Nb. The high temperature Gorsky effect measurements will be extended to other metal-hydrogen systems.

If the initial experiments on helium diffusion are successful, this phase of the work will be increasingly emphasized. Attention will be focused on the diffusion of interstitial He and its interactions with specific trapping sites. The transition from interstitial He to He gas bubbles will be studied using both resistivity and anelastic piezoresistance methods.

The Raman studies will continue to be applied to characterization of the vibrational modes of H(D) in solution and of surface adsorbed molecules (H₂S). The local lattice phonon spectra near the interstitials will be probed using these techniques. In addition the data should yield information about the high temperature diffusivity. Examination of the optical scattering in the temperature-composition region near the miscibility gap should yield information about the decomposition of the solid solution. Clustering of the hydrogen solutes should be measurable with the optical methods and will provide a powerful method for studying the spinodal decomposition of the solid solution.

Relationship to Other Federally Funded Projects: This program is closely correlated with an ONR sponsored program which is directed toward a study of hydrogen embrittlement in bcc metals. The mechanisms of fracture are being studied in the same systems in which the hydrogen mobility is being determined. As the studies of surface adsorption effects on hydrogen entry develop it is expected that these will also be paralleled by fracture studies.

The Raman studies of H in metals is a joint program with M. Klein of the MRL whose part of the program has been supported by ARPA. The interaction has brought together a strong metallurgical group and a strong light scattering group which are examining a series of problems which would be difficult for either group to study alone.

The hydride precipitation is a joint effort with Hamish Fraser of the MRL whose work is supported by ERDA.

The helium interstitial measurements are being carried out at the University of Illinois but the specimen doping with ^3H is being performed at Battelle Northwest by Dr. A. B. Johnson of the Corrosion Research Division. The project will be a joint one with Dr. Johnson's group.

The continuation of our studies of H in Fe will be a joint effort with Professor M. Bernstein of the Carnegie-Mellon University who has been studying the effects of substitutional solutes on H embrittlement of steels.

Close coordination of the program is maintained with the NMR measurements of hydrogen mobility in niobium of Professor T. Rowland with ERDA support, with the theoretical studies of quantum mechanical diffusion mechanisms of Professor C. P. Flynn with NSF support, with the ultrasonic investigation of hydrogen in metals of Professor A. Granato with ERDA support and the ERDA supported program of fracture of Professor N. Pugh.

Publications: (Calendar Year 1975)

H. K. Birnbaum and H. Wadley
Hydrogen Embrittlement of Molybdenum
Scripta Metallurgica 9, 1113-1116 (1975)
Also supported by the United Kingdom Atomic Energy Establishment at Harwell

R. F. Mattas and H. K. Birnbaum
Isotope Effects on the Motion of O-H Clusters in Nb
Acta Metall. 23, 973-977 (1975)

M. F. Bluem and H. K. Birnbaum
Determination of the Thermally Activated Deformation Parameters in Nb and Nb-N Alloys
Proceedings Int'l. Conf. on the Strength of Metals, France, 1976 (to be published)

M. L. Grossbeck, Peter Williams, Charles A. Evans, Jr., and H. K. Birnbaum
Application of Ion Probe Analysis to Studies of Hydrogen Behavior in Solids
Phys. Status Solidi A (in press)

Also supported by NSF

Peter Williams, Charles A. Evans, Jr., Martin L. Grossbeck, and Howard K. Birnbaum
Ion Microprobe Analysis for Niobium Hydride in Hydrogen-Embrittled Niobium
Anal. Chem. (in press)

Also supported by NSF Grants DMR-72-03026 and MPS-72-05745 and
ONR N00014-67-A-0305-0020

M.S. Theses: (Calendar Year 1975)

None

Ph.D. Theses: (Calendar Year 1975)

None

Applications of Electron Microscopy in Materials Science

Principal Investigator: Hamish L. Fraser, Ph.D.
Assistant Professor of Metallurgy

Supporting Agency: U. S. Energy Research and Development Administration

Senior Staff: Hamish L. Fraser, Assistant Professor

Junior Staff: Scott E. Hughes, Research Assistant (Term 9/20/75)
Nestor J. Zaluzec, Research Assistant

Object: The principal aim of the proposed research is to apply the techniques of electron microscopy to studies in materials science. As such the program is divided into two sections. One part consists of an investigation of the omega phase transformation in Zr-Nb alloys using analytical and high resolution electron microscopy. The second represents a change in emphasis in the current research program from studies of elevated temperature deformation of β -NiAl single crystals to those involving the determination of mechanisms of environmentally-induced failures in structural materials, and is a part of a more comprehensive study presently in progress at this University.

In the case of the studies of the omega phase transformation in Zr-Nb alloys, the aim of the current experiments is to use the most recent analytical techniques in electron microscopy to derive a more detailed understanding of this type of phase transition. Many of these new techniques are not well developed and it has been necessary to perform a number of experiments which have led us to the point where we are now able to apply these techniques with some degree of confidence. Specifically, imaging of defects and micro-area diffraction using scanning transmission electron microscopy and quantitative microchemical analysis of thin foils by the use of energy dispersive analysis of X-rays have been studied. The results of these preliminary studies will be described in "Results, FY 76", but it is worth noting that simple application of the available techniques without careful analysis of the results may lead to errors in characterization.

The study of the omega phase transformation has resulted from the interaction of the principal investigator and Professor H. E. Cook of the Departments of Mechanical and Metallurgical Engineering. Cook is well known for his theoretical description of the omega phase transformation, and it is one aim of the current experiments to check the predictions that result from his theories.

The omega phase transformation has been the subject of much study over the last decade. Originally, the transformation was characterized by the use of X-ray diffraction techniques. More recently, electron microscopy has been utilized to obtain not only diffraction data but also some direct observations of the transformation products. The observations made to date indicate that, on quenching from the bcc solid solution phase field to room temperature, the omega phase precipitates in the form of very small particles ($\sim 15 \text{ \AA}$) with a spacing of $\sim 25 \text{ \AA}$ between particles.

Moreover, the images of these particles are not stable with time but are repeatedly forming and disappearing. The suggestion has been made that omega particles are continually transforming to the bcc phase and then reverting back to the hcp omega phase. It is felt that more experimental work is needed to clarify this point. The proposed work on the omega phase transformation would involve a critical experimental review of the microstructures pertaining to thermal and athermal transition products. The structures will be analyzed using high resolution and analytical electron microscopy.

The second part of the proposed program consists of studies related to environmentally-induced failures in structural materials and is thus part of the comprehensive study of such failures currently in progress at Illinois. Professor H. K. Birnbaum and his research group have performed experiments to determine the mechanism of hydrogen embrittlement in Nb-H alloys. The results of their work indicate very strongly that the fracture of a hydride formed ahead of the crack tip is responsible for the embrittlement. In view of this, a joint program was initiated with the aim of observing the morphology and determining transformation mechanisms of the hydride in Nb-H alloys using analytical electron microscopy. Precipitation of hydrides in thin and thick foils from the solid solution is being studied. Further, the effects of varying the method of hydrogen charging are also being determined.

In addition to these studies of hydride precipitation in Nb-H alloys, a comprehensive study of the embrittlement of Zr and its alloys by iodine is planned. Such embrittlement has been observed in reactor environments, but has not been characterized to any great extent. In view of its relevance to the other studies on environmentally-induced failures in structural materials currently in progress, it is planned to perform a detailed study of this embrittlement phenomenon. One possible mechanism of embrittlement is the brittle fracture of an iodide at the crack tip, so that a detailed study of fracture faces using the electron microprobe and Auger spectrometer will be made. In addition, the possibility of forming iodides in these alloys will be studied using analytical electron microscopy to examine thin foils which have been reacted with iodine vapor.

Results, FY 76:

Most Significant Accomplishments: During work aimed at determining increases in usable foil thickness when using scanning transmission electron microscopy, foils of Si containing stacking faults were irradiated with 200 keV electrons. It has been shown in this work that such electrons are sufficiently energetic to displace Si atoms from the lattice, with the result that interstitial defects are nucleated at the stacking faults. Previous estimates of the threshold voltage for displacements of Si atoms by electrons was significantly higher than this value; this difference is probably due to the presence of the stacking faults acting as nucleating sites for the interstitials produced by electron irradiation.

Other Results: The main emphasis of our work during FY 76 has been to develop a number of techniques in analytical electron microscopy. Specifically, in the case of scanning transmission electron microscopy (STEM), it has been determined that, contrary to expectations quoted in the literature, for crystalline materials no increase in usable foil thickness is realized when using STEM. This led to the determination of the limitations to usable foil thickness in conventional transmission electron microscopy (CTEM), particularly light elements. It has been found that either finite angle inelastic scattering effects, or inelastic scattering involving loss of contrast limits usable foil thickness. Thus, while the effects of chromatic aberration are important, they are not limiting in the case of thick foils in CTEM. In the case of application of energy dispersive analysis of X-rays generated in thin foils, advances in data reduction have been made. A background subtraction and profile fitting computer program has been developed from first principles, and this computer program is being used to provide quantitative microchemical analysis in thin foils. One assumption that must be made when applying quantitative analysis methods is the fact that the ratio of peak intensities of two elements be independent of foil thickness. We have checked this using an homogeneous foil of NiAl, and observed a variation in this ratio. Part of this variation is attributed to differences in excitation and absorption of X-rays with atomic number and foil thickness; whereas in very thin parts of the foil, the spectrum is dominated by X-ray fluorescence excited by Bremsstrahlung produced at various points in the electron optical column. The Bremsstrahlung effect can be minimized by using special column liners, and the other effects can be predicted, and thus corrected for, by calculation.

Results Expected, FY 77: On the work concerning the omega phase transformation in Zr-Nb alloys, it is expected that the equilibrium structure will be determined experimentally. This structure will be compared with that predicted by theory. Furthermore, thermal cycling between room temperature and 77 K should result in the formation of relatively large omega particles, and these will be studied in the electron microscope. These structures will be compared with that produced by slow furnace cooling.

In the case of hydrides in Nb-H alloys, the in situ cooling experiments will be continued. There have been some problems associated with the formation of oxide particles in our alloys; it may be possible to identify the oxides using electron energy loss measurements and such a determination will be attempted. The experiments on hydride precipitation will be extended to cover the spinodal decomposition occurring at the miscibility gap.

Experiments to characterize the fracture of Zr and Zr alloys in an iodine environment will be started. Auger spectroscopy, electron microprobe analysis, scanning electron microscopy and analytical electron microscopy will all be used in this characterization. Particular attention will be paid to crack tip processes.

Results Expected, FY 78: It is conceivable that satisfactory results will have been obtained from the work on the omega transformation. It is planned to terminate this project and reorientate the research into some aspect of environmentally-induced failure to accentuate the thrust that is being developed on this subject in MRL and Metallurgy.

The work on hydride precipitation should be expanded to other systems such as Ta-H alloys where, compared to the case of Nb-H alloys, not only do phase diagram differences exist but also the degree of hysteresis accompanying thermal cycling is much reduced.

Work will continue on the embrittlement of Zr and Zr alloys by iodine. By the end of this year, a fairly comprehensive understanding of the failure mechanisms should be developed.

Relationship to Other Federally Funded Projects: A number of interactions between this project and others on campus have been developed. The work performed in this program may be divided into three major areas, namely the omega phase transformation, environmentally-induced failures, and development of some new techniques in analytical electron microscopy. With regard to the omega phase transformation, as described above, this work is being performed in cooperation with H. E. Cook (supported by the University of Illinois). The interaction stems from the complementary nature of our two contributions--namely the theoretical input from Cook and the experimental input from the principal investigator. Other federally funded work on the omega phase transformation exists, probably the most significant being that of Professor S. Sass at Cornell University (funded by ONR).

In the case of the environmentally-induced failures, a number of strong interactions exist. The work on hydride precipitation in Nb-H alloys is a cooperative study with H. K. Birnbaum (supported by ONR). The study of embrittlement of Zr and its alloys by iodine enjoys the interaction of E. N. Pugh. Furthermore, a strong interaction occurs between myself and Pugh over his work on hydrogen embrittlement and stress corrosion cracking of Mg (supported by ERDA). In this work, my contribution concerns the application of transmission electron microscopy to study specimens prepared from the fracture surfaces. Finally, the principal investigator is a member of the group of researchers carrying out a study to determine the mechanisms of hydrogen embrittlement in stainless steels and nickel-iron alloys (supported by NSF).

Other interactions exist through the expertise that has been developed in conventional transmission electron microscopy and analytical electron microscopy. Interactions exist between the principal investigator and (1) C. M. Wayman (NSF-funded) where the nature of the phase transformations in β -brass are being determined by use of the energy dispersive X-ray analyzer; (2) J. E. Greene (Joint Services Electronic Program funded) where the microstructure of thin semiconductor films

grown by sputter deposition is being determined; (3) R. Mehrabian (ARPA funded) where microanalysis of interfaces in composite materials using analytical electron microscopy is being performed; (4) C. A. Wert where elemental and structural changes accompanying carbide precipitation in V-Ti-C alloys are being studied.

Publications: (Calendar Year 1975)

Hamish L. Fraser and Ian P. Jones

A Note on the Increase in Usable Foil Thickness in Scanning Transmission Electron Microscopy

Phil. Mag. 31, 225-228 (1975)

H. L. Fraser, N. J. Zaluzec, J. B. Woodhouse, and L. B. Sis

On the Feasibility of Quantitative Microchemical Analysis of Thin Metal Foils
33rd Annual Proceedings Electron Microscopy Society, G. W. Bailey, ed. (Las Vegas, Nevada 1975) pp. 106-107

M.S. Theses: (Calendar Year 1975)

Scott E. Hughes (H. L. Fraser, Adviser)

A Preliminary Study of the Morphology of Hydride Precipitation in Tantalum
October 1975

Ph.D. Theses: (Calendar Year 1975)

None

Deformation of Reinforced Metals

Principal Investigator: Marvin Metzger, Ph.D.
Professor of Physical Metallurgy

Supporting Agency: U. S. Energy Research and Development Administration

Senior Staff: Marvin Metzger, Professor

Junior Staff: Prabir R. Bhowal, Research Assistant

Object: The objective of this work is to develop realistic models of the mechanical behavior of metal-matrix fiber or lamellar composites based on observations of dislocation structures. The central question concerns the principles governing the behavior of the matrix and the nondeforming phase as affected by their interaction during straining. General macroscopic formalisms for composites are now well known but these do not take account of how the properties of the individual components are altered by interaction and how the nature of the interaction might be predicted from the elastic and plastic properties of the components. This question must be answered for effective prediction of composite behavior in regard to strength and ductility and the design of structure, e.g., how does one predict the optimum interlamellar spacing and would the benefits of attaining it justify an extraordinary effort in processing. The question has heretofore received less attention than it deserved because attention in composites have been directed mainly toward finding compatible fiber-matrix combinations, methods of effective or economical processing and the general properties of the product and also because of certain experimental difficulties with many composites--e.g., chemical incompatibility of the components which prevents proper thinning for electron microscopy. The objective of this work is best realized by concentrating on model systems which fit experimental requirements, which include close spacing of the reinforcing phase, ability to vary the spacing and amenability to thinning for microscopy. Current efforts deal with the $\text{Ni}_3\text{Al-Ni}_3\text{Nb}$ aligned eutectic composite which satisfies these requirements and has further advantages as a model material in that the operative slip modes of the matrix change with temperature; these outweigh its experimental disadvantage of relatively low ductility. Although this material would be classed as a high temperature alloy, the information developed will be of general and not merely of specific value.

Results, FY 76:

Most Significant Accomplishments: From intensive study of dislocation structures to 600°C , blocked slip band (pile-up) or image force models were definitely ruled out and the matrix-reinforcing phase interaction was shown to be dominated by interface strain compatibility requirements. The availability of slip modes able to accommodate this requirement was found to control changes in stress-strain behavior and ductility with temperature.

Other Results: A number of specific modes of dislocation cross-slip and reaction were identified. These, most of which have not previously been described, account for production of dislocation debris and explain why the matrix strain hardens so rapidly. Faults and dislocations in the Ni_3Nb reinforcing phase were identified. The importance of these details is that in real composites stress and strain are inhomogeneous and their properties can not be correctly treated on the basis of uniform deformation.

Results Expected, FY 77: In this period we expect to deal specifically with the question of mechanical behavior and dislocation structure versus interlamellar spacing, working with composites having both larger and smaller spacings than the 2 μm material currently under study. In the absence of detailed mechanical and microstructural information, the model of a blocked slip band leading to the Hall-Petch relation is often used to conceptualize this question. However, we will be especially looking to develop a formalism for predicting the variation of flow stress with interlamellar spacing based on a more realistic model. A smaller effort will be made to extend previous observations to temperatures above 600°C, the interactions at the higher temperatures being of interest theoretically to analyze the behavior as the matrix passes through its maximum in strain hardening rate.

Results Expected, FY 78: We expect to continue along the present lines to test the principles developed to this point by examining their applicability with another model composite in which matrix deformation modes are different and fewer in number. Composites which possibly satisfy the theoretical and experimental requirements are being looked at. Processing to the desired structure is a strong consideration here, and preliminary discussion has been instituted with researchers having expertise and interest in processing to explore areas of common interest.

Relationship to Other Federally Funded Projects: Current work interacts with certain work in Dr. F. D. Lemkey's group at United Technologies Research Center, East Hartford, Conn. Their efforts, company-sponsored, are in development of aligned eutectic composites for high temperature service. They are able to prepare for us special alloys with the structure required for our studies, and information is exchanged on these alloys and related topics. Local interactions are with groups like those of H. Fraser and A. Granato who are concerned with dislocation properties.

Publications: (Calendar Year 1975)

M. Metzger

Intergranular Corrosion of Single Phase Aluminum as Pitting Phenomenon
Journal de Physique 10, C4-387-393 (1975)

Also supported by ARO(D)

M.S. Thesis (Calendar Year 1975)

James G. Sheltens

Scanning Electron Microscope Study of Pitting on Aluminum in Sulfuric Acid
Containing Chloride

1975

Also supported by ARO

Ph.D. Theses: (Calendar Year 1975)

None

The Mechanism of Stress-Corrosion Cracking: Propagation Studies

Principal Investigator: E. Neville Pugh, Ph.D.
Professor of Metallurgical Engineering

Supporting Agency: U. S. Energy Research and Development Administration

Senior Staff: E. Neville Pugh, Professor

Junior Staff: Gerhardus H. Koch, Research Assistant (Term 2/27/76)
Joseph L. Nelson, Research Assistant

Object: This research is part of a broad study at the Urbana-Champaign campus of the mechanisms of environmentally-induced fracture of structural materials. These failures, particularly stress-corrosion cracking (SCC) and hydrogen embrittlement (HE), occur widely in the present generation of nuclear reactors, frequently with serious consequences. Thus SCC of nickel base (e.g., steam generators) and copper base (e.g., condenser tubes) alloys have led to extended shut-downs; similarly, the cracking of austenitic stainless steels has been a common and costly event in various locations within nuclear plants. Both zirconium and magnesium alloys, used as fuel cladding materials, are also susceptible to SCC and HE. These failures were reviewed at a recent ERDA workshop (Germantown, February 24-25, 1976). Significantly, it was clear that similar failures can be anticipated in future types of reactors and in other developing energy industries, particularly in coal gasification and in the harnessing of geothermal energy.

Efforts to combat environmentally induced fractures are hindered by our lack of understanding of the underlying mechanisms. While some uncertainty remains, it seems that SCC can be grouped into two distinct classes, intergranular (I-SCC) and transgranular (T-SCC). The mechanism of the former is relatively well understood in broad terms, and almost certainly occurs by preferential anodic dissolution of film-free metal at the crack tip, exposed by localized plastic deformation, while the crack walls (non-deforming) remain protected by a passive film. The intergranular path of cracking is thought to result from slower repassivation of grain boundaries compared to that of the grain centers, but the factors which determine the repassivation characteristics of grain boundaries remain to be established.

T-SCC is poorly understood at present. Fractographic studies indicate that the failures occur by cleavage, that is, by brittle mechanical fracture, and thus the mechanism is considered to be basically different from that of I-SCC. The cause of embrittlement has not been established, but there is considerable interest, and controversy, in the possibility that it is due to hydrogen absorption--that is, that T-SCC is a form of HE. It is well established that HE occurs in certain materials, e.g., high

strength steels and the refractory metals such as vanadium and niobium, and that it can result from internal hydrogen, introduced by cathodic or high-temperature gas charging, or during exposure to external gaseous hydrogen. Two mechanisms of HE are currently being advocated, the first postulating that hydrogen reduces the bond strength of the host material (decohesion model), and the second proposing that cracking proceeds by the formation and fracture of brittle, stress-induced hydrides. It is possible that each of these mechanisms may operate in particular cases, or, alternatively, that only a single mechanism is responsible for all cases of HE.

The present project is concerned primarily with the mechanism of T-SCC, and, because of the possible involvement of hydrogen, with that of HE. The studies are being carried out on the HCP alloys of magnesium, titanium and zirconium, and on an Al-Zn-Mg alloy. Currently, the main experimental techniques are fractography and acoustic emission, the latter being used to investigate the important question of whether crack propagation is continuous or discontinuous.

Results, FY 76:

Most Significant Accomplishments: The most significant finding was made in studies of SCC and HE of a Mg-Al alloy. Our earlier studies have shown that this alloy undergoes cleavage-like T-SCC in aqueous chloride-chromate solutions, and also fails transgranularly by internal hydrogen embrittlement (IHE) after exposure of unstressed specimens to this solution, and by gaseous hydrogen embrittlement (GHE). In the past year, SEM and electron-diffraction studies have shown that a brittle layer of MgH_2 exists at the fracture surfaces produced by SCC, IHE and GHE. Tests in which clean surfaces, produced by rapid ductile fracture in the environment, were exposed to the aqueous or gaseous environment provided no evidence of the hydride, suggesting that it is stress-induced during slow crack growth in SCC and both forms of HE. These observations are of particular significance since they suggest that T-SCC, in this system at least, is a form of HE, and that it involves the formation of stress-induced hydrides.

Significant progress has also been made in the study of Ti-8Al-1Mo-1V, a "near- α " commercial alloy containing ~5 percent β . GHE was found to occur in 1 atmosphere dry hydrogen in specimens containing continuous β , but not in those in which the β phase is discontinuous. Cracking was observed to follow the α - β interface and electron-microscope (SEM and TEM) and electron-diffraction studies established the presence of a brittle layer of TiH_2 at the fracture surfaces. The solubility and diffusivity of hydrogen is considerably greater in β - than in α -Ti, and thus our observations support the view that hydrogen enters via the β , forms the brittle hydride in the α at the α - β interface, and permits crack propagation through this brittle phase. Fractographic and acoustic-emission studies indicated that propagation is discontinuous.

Other Results: A study has also been made of the SCC of Ti-8Al-1Mo-1V. The alloy underwent cracking in aqueous chloride solutions but the characteristics of failure were significantly different from those of GHE. Thus cracking in aqueous solution occurred in specimens in which the β -phase was either continuous or discontinuous, and took place by $\{10\bar{1}7\}$ cleavage through the α -phase rather than following the α - β interface. Electron diffraction provided no evidence for the presence of hydride at the stress-corrosion fracture surfaces, and thus it can be seriously questioned whether hydrogen plays any role in the stress-corrosion fracture process. On the other hand, it is possible that hydrogen is able to directly enter the α -phase from the aqueous solution (pH $\sim$ 1.7), and because of the higher fugacity, that it precipitates as a surface layer of hydride which is too shallow to be detected by our electron-diffraction technique. Such a layer might conceivably lead to embrittlement of the α -phase, but it is clear that further work is necessary to provide support for a hydrogen model in this system.

We have continued our studies of SCC of an Al-Zn-Mg alloy. This alloy generally cracks intergranularly, but our work during the past year established that T-SCC can occur if I-SCC is avoided. The transgranular fracture surfaces have been shown to be cleavage-like, similar to those in other cases of T-SCC, and the presence of striations indicate that propagation is discontinuous. Significantly, observations to date suggest that the failure results from the entry of hydrogen generated by reaction of water with aluminum.

Results Expected, FY 77: It was seen in the preceding section that SCC and HE in the Mg-Al alloy were found to be associated with the formation of MgH_2 . Further progress in understanding the mechanism of these failures requires a more detailed knowledge of the structure and morphology of the hydride layers at the fracture surfaces, and of hydride precipitation in this alloy, per se. These aspects are now being investigated by transmission electron microscopy in collaboration with H. L. Fraser. It is hoped that these studies will resolve several apparent anomalies which currently exist. For example, SCC in this alloy occurs by cleavage on $\{31\bar{4}0\}$ planes, whereas IHE and GHE produce transgranular fracture surfaces which are uneven on a microscopic scale, exhibiting a corrugated appearance, and which do not tend to be in $\{31\bar{4}0\}$ planes. It may be speculated that these differences result because fracture in SCC occurs on the cleavage plane of a thick hydride, but that the HE processes involve cracking along the habit planes of thin plates.

It is anticipated that the characterization of T-SCC in the Al-Zn-Mg alloy will be completed in FY 77. In particular, we expect to obtain the orientation of the fracture plane, and to compare it with those for T-SCC in the other FCC alloys, α -brass and austenitic stainless steel, which are being determined in parallel programs (see Relationship to Other Federally Funded Projects). It is hoped that some generalizations will emerge. It was seen above (FY 76) that the fracture surfaces of this

alloy are striated, indicating that propagation is discontinuous. Acoustic-emission studies are in progress to provide further evidence for this important conclusion. In addition to providing evidence for discrete emissions, this technique allows the determination of the time intervals between crack-advance events. Thus knowing the crack-advance distance from fractography, i.e., the interstriation spacing, an estimate can be made of the overall crack velocity which can be compared with directly measured values. Such a comparison would provide an important test of our views.

In FY 77, we plan to begin an investigation of the failure of zirconium alloys in iodine vapors at elevated temperatures. This is a transgranular failure which has occurred in zircaloy fuel cladding, iodine being a fission product, but the prime motivation for these studies is mechanistic and relates to the role of hydrogen in embrittlement phenomena. It is considered that the occurrence of HE in a wide variety of materials stems from the fact that hydrogen is present in commonly encountered environments and also because it is highly mobile in metals at ambient temperatures. Thus similar embrittlement might be expected to result from certain other species if they were present in sufficient concentration and if they were sufficiently mobile. The iodine-induced cracking of zircaloys is thought to be an example of such a failure. Because of our interest in the possible role of hydrides in HE and T-SCC, a prime objective will be to identify iodides in failed specimens by means of transmission electron microscopy and electron diffraction. These studies will again be carried out in cooperation with H. L. Fraser. An advantage of this approach is that iodine can be detected by electron-optical techniques, e.g., the microprobe and Auger spectroscopy, in contrast to hydrogen.

Results Expected, FY 78: It is evident from the preceding sections that the program is moving logically into a study of the role of stress-induced hydrides in embrittlement phenomena. Thus it is anticipated that effort in FY 78 will be centered increasingly on the study of hydride formation in a number of materials, including α -titanium, Mg-Al and possibly Al-Zn-Mg.

Relationship to Other Federally Funded Projects: It was seen in a preceding section (Object) that there are several forms of environmentally induced fracture, I-SCC, T-SCC and HE. Both forms of SCC occur in α -brasses in aqueous ammonia and are being studied by the Principal Investigator (and two research assistants) under an ARO grant. The Principal Investigator, sharing a postdoctoral fellow with C. J. Altstetter, is also taking part in a NSF-funded study of T-SCC and HE of austenitic stainless steels; this is part of a larger, interactive program on the HE of Fe-Ni-Cr alloys (with H. K. Birnbaum, H. L. Fraser and R. A. Yeske). The phenomenon of HE is also being studied by H. K. Birnbaum in niobium, and there is useful interaction between this work and the present project. The Principal Investigator is also developing strong interaction with H. L. Fraser on transmission electron microscopy of hydrogenated foils, and with R. A. Yeske on the fracture-mechanics approach to the characterization of crack propagation. It is anticipated that further interaction will develop

with a new faculty member, R. Mehrabian, on the influence of new processing methods on stress-corrosion behavior; for example, we plan to pursue the effects of melting and rapidly solidifying shallow surface layers by means of laser heating. Thus it is evident that a significant thrust is being developed in the area of SCC and HE. Further, these studies are part of a broader program within the MRL on the behavior of hydrogen in metals.

Publications: (Calendar Year 1975)

D. G. Chakrapani and E. N. Pugh
The Transgranular SCC of a Mg-Al Alloy: Crystallographic, Fractographic and Acoustic-Emission Studies
Metall. Transactions 6A, 1155-1163 (1975)

D. G. Chakrapani and E. N. Pugh
On the Fractography of Transgranular Stress-Corrosion Failures in a Mg-Al Alloy
Corrosion 31, 247-252 (1975)

J. L. Nelson and E. N. Pugh
The Occurrence of Transgranular Cleavage-Like Fracture in an Al-Zn-Mg Alloy During Tensile
Metall. Transactions 6A, 1459-1460 (1975)

H. Gabel, J. A. Beavers, J. B. Woodhouse, and E. N. Pugh
The Structure and Composition of Thick Tarnish Films on Alpha-Phase Copper Alloys
Corrosion (accepted)
Also supported by ARO-D-G127

D. G. Chakrapani, G. H. Koch, and E. N. Pugh
On the Mechanism of SCC in a Mg-Al Alloy
Proceedings Sixth International Congress on Metallic Corrosion, Australia, 1975
(to be published)

D. G. Chakrapani and E. N. Pugh
Hydrogen Embrittlement in a Mg-Al Alloy
Metall. Transactions (accepted)

M.S. Theses: (Calendar Year 1975)

None

Ph.D. Theses: (Calendar Year 1975)

D. G. Chakrapani (E. N. Pugh, Adviser)
Transgranular Stress-Corrosion Cracking of a Magnesium-Aluminum Alloy
May 1975

Precipitation in Refractory Metal Alloys

Principal Investigator: Charles A. Wert, Ph.D.
 Professor of Physical Metallurgy;
 Head, Department of Metallurgy and Mining Engineering

Supporting Agency: U. S. Energy Research and Development Administration

Senior Staff: Charles A. Wert, Professor

Junior Staff: Stephen H. Brummer, Research Assistant
 Theodore R. Wilken, Research Assistant (Term 1/22/76)
 Dennis Beggs, Research Assistant

Object: The refractory metal compounds--oxides, nitrides, carbides and hydrides--are important in bulk, but they are even more important as inclusions in metals since they control many of the mechanical properties. A wide variety of compounds exists and the available ranges of composition and temperature are so great that extreme selectivity must be exercised to keep experiments within bounds. Three specific problems have been tackled in the past five years, two of which are still active and one of which has reached a stage of completion. The first is concerned with carbides in V and Nb, the second with hydrides in V, Nb and Ta and the third with oxides of W.

Carbides in vanadium and niobium are important hardening agents. Nearly twenty years ago, carbides in niobium were found to give excellent high temperature strength; my first introduction was in association with the Pratt and Whitney nuclear-powered aircraft project. In that work, there was no time to do anything but try a wide series of alloys and no detailed micro-structural examination of carbide-hardened alloys was made.

Later we began to examine carbide formation in binary alloys of vanadium and carbon. Rapid quenching of alloys carbonized above 1000°C permits appreciable quantities of carbon to be retained in solution (up to 0.5 at.%). Aging in the temperature range 200-800°C produces a sequence of two carbides. The first is a fine-scale coherent carbide on (310) habit planes of the host metal. Formation of this carbide is accompanied by appreciable strengthening of the alloy. Prolonged aging above 500°C results in transformation of this carbide to the hexagonal V₂C, whose basal plane attempts to match the (110) plane of the host metal. Even though considerable mismatch occurs on this plane, the alloy is soft in this state, and the binary V-C and Nb-C alloys are not practical for high temperature service.

Ternary alloys V-Ti-C are now being examined to determine the crystalline nature of the carbides and the range of effective age-hardening. Alloys of 1%, 5% and 15% Ti have been prepared, carburized and examined partially. Alloys at 1% Ti are little different from the plain binaries, so no further work is planned for this composition.

Alloys of 5% Ti produce a striking new effect--a high temperature carbide, coherent on (100) planes, is formed around 1000°C, where it is remarkably stable. Three types of investigation are under way: (1) chemical analysis of the carbide is being attempted using the non-dispersive detector of the electron microscope, (2) the range of stability over time and temperature is being determined, and (3) mechanical properties of the alloy will be measured as a function of aging times and temperature.

The important feature of this alloy is the possibility that finely-dispersed coherent carbides may be formed in vanadium at temperatures well over $T_m/2$. Similar effects may be seen in Nb-Ti-C alloys. We expect to extend the work to higher concentrations of Ti and to quaternary alloys such as V-Ti-Cr-C. The path to go has been well explored by Professors Jack of Newcastle-on-Tyne and Honeycombe of Cambridge, who have shown remarkable strengthening of the bcc iron phase of low-alloy steels hardened by judiciously chosen nitride and carbide precipitates.

Alloys of Nb and V are certain eventually to be important in high temperature service, so the nature of the carbides which strengthen them and ranges of composition, temperature and compatibility with hydrogen must be determined.

Results, FY 76:

Most Significant Accomplishment: Refractory metal compounds, especially oxides, are important in industrial production of metals and alloys. Because of wide diversity in composition and stability of oxides, conditions of oxide reduction to the metallic state are almost unique material by material. We have concluded a study of reduction of tungsten oxide to tungsten metal over a wide range of reduction conditions and of additives found useful in commercial practice. The work results from a long series of investigations between C. Wert and the Westinghouse Lamp Division on production of lamp filaments. The present work is a collaborative effort between H. Sell and W. Morcom of Westinghouse with C. Wert, Ted Wilken and J. Woodhouse of the University of Illinois. It was a massive study--some 700 oxide and metal powders were examined.

Commercial tungsten for filaments is nearly pure tungsten--it contains only a few hundred ppm of potassium, silicon and aluminum. Even so, these additives are important in the development during processing of an interlocking elongated grain structure which strengthens the filament. The metallic elements are added as oxides and salts at an intermediate processing stage--usually when the tungsten is an oxide or a paratungstate.

This investigation had the goal of determining the nature of intermediate steps during the reduction of WO_3 to α -W and the role of the dopant compounds of K, Si and Al. Observations were made of the stoichiometry, crystal structure and appearance of both intermediate oxides and the final nearly-pure metal. Observational techniques included chemical analysis, analysis of the reducing gas, X-ray structure determinations and scanning electron microscopy.

Starting materials were all basically $W_{20}O_{59}$, a slightly off-stoichiometry WO_3 . Five different materials were used: "pure" $W_{20}O_{59}$, the oxide "commercially-doped" with compounds of K, Si and Al, and the oxide doped selectively with either SiO_2 , Al_2O_3 or K_2SiO_4 . All reductions were carried out over the range 500°C to 900°C in hydrogen gas of controlled initial water vapor content.

Three main reduction paths are observed.

This reaction occurs at lower temperatures and for the purer materials. It is not of practical importance.

This reaction occurs at intermediate temperatures and is of marginal practical importance.

This is the important reduction path for production of commercial tungsten powder.

The end-product $\alpha-W$ of process 3 is the most important practically. It produces metallic crystallites of a mixture of sizes. Importantly, the larger crystallites do not possess smooth facets, but are dimpled and rough. We believe that the potassium-aluminum-silicon compound important to high-temperature creep resistance of lamp filaments is carried along in these dimples and holes developed during reduction.

Sorting out the myriad of observations and establishing valid general conclusions has been an enormous task. But it is now completed and we intend to begin on the next stage--determination of the nature of the important potassium-bearing compound present in the crystallites. This problem is referred to again in FY 78.

Results Expected, FY 77: Three areas are ripe for further investigation:

- (a) Carbide strengthening of ternary and quaternary alloys of V and Nb.
 - (b) Resolution of discrepancies in thermodynamic and kinetic features of the V-H and V-D alloy systems.
 - (c) Extension of dopant techniques strengthening of W to other bcc metals.
- During FY 1977 we expect to work on the first two of these.

Ranges of stability of coherent fine-scale mixed carbides will be determined in V. These alloys will be made by carburizing specimens of appropriate Ti and Cr composition, followed by quenching and aging in the temperature range 1000°C to above 1200°C. Concentrations of Cr and Ti will be in the range 5 to 15 at.%. The effect of these carbides on the high temperature strength will be determined.

Experiments in alloys of iron containing precipitated nitrides such as $(\text{Fe}_x\text{Mo}_y)_{16}\text{N}_2$ and $\text{Fe}_x\text{V}_y\text{C}$ have shown that appreciable strengthening of the bcc matrix occurs for precipitates in the sub-micron range. The carbides are the more effective as the particle size decreases. In the ferritic steels, precipitates as small as 20 Å in size can be produced, partly by use of the γ - α transformation. Appreciable strengthening occurs to temperatures of 600°C to 800°C. We can produce carbides as small as these in V even without the aid of a γ - α transformation. But we are aiming at much higher temperatures and may have difficulty preventing carbide coarsening and consequent softening. But the strong tendency for the alloy to choose a carbide of such composition that near-coherency of lattice matching occurs gives hope that success can be achieved at least to 1000°C.

Results Expected, FY 78: An attractive prospect is the strengthening of bcc metals other than tungsten by "void" hardening. Especially attractive is the possibility of improvement in high temperature creep resistance by immobilization of grain boundaries.

Tungsten lamp filaments contain elongated grains stabilized by "voids". These voids, however, are not simply collections of vacancies; they are filled with potassium carried over in some manner from the early stages of reduction of the doped oxides. Potassium must be nearly insoluble at high temperatures and the voids are produced on the first heating of a filament by volatilization of particles of potassium metal or a potassium compound which is above its critical point.

Can this be done for other bcc metals? The metallurgy is formidable. Conditions and levels of dopant must be found. The oxides must have the correct level of stability to permit reduction at temperatures low enough so that the dopant is not fully volatilized during production of the metal. Then the crystallites of metal powder must apparently have holes or dimples sufficiently deep to trap the dopant during the sintering steps.

The first metal to try is vanadium. Its oxides have relatively low stability in contrast to those of niobium and tantalum, which are quite stable. Even for vanadium, the task is formidable. Some forty years of commercial practice brought tungsten to its present state and some fifteen years of investigation were required to understand the hardening mechanism. But once the transmission electron microscope, the scanning electron microscope and the Auger spectrometer were brought to bear on the subject, the answer came quickly.

With this background of understanding, we should be able to see if the technique has any promise for other bcc's in a reasonable time.

Relationship to Other Federally Funded Projects: Hydrogen, deuterium and tritium are important to the use of refractory metals. They have huge solubility at high temperatures in V, Nb and Ta and cause embrittlement. At low temperatures where hydrides (deuterides and tritides) form,

embrittlement is even more of a problem, even at low gas concentrations. In other metals such as W, Mo and many steels, hydrogen may be sparingly soluble, but may cause embrittlement even so.

My interest in these problems developed in the late 1960's from two sources:

- (1) A long series of discussions with C. P. Flynn and M. Stoneham as they developed a diffusion theory particularly applicable to light elements.
- (2) Several summers at the Science Center of Rockwell International where we began to work on mechanical aspects of alloys containing hydrogen--partly because of the interests of Rocketdyne in high pressure storage of hydrogen and its use as a fuel in space vehicles.

Almost at the same time H. Birnbaum developed an interest in hydrogen diffusion and gradually the activity at Urbana has grown to include many metallurgy and physics faculty. My continuing part of this activity within MRL is now only modest (one graduate student) and is centered in trapping of hydrogen by oxygen, nitrogen and carbon atoms in V and Ta. This is accomplished by determination of the effect of impurity additions (in the range 0.1 to 1.0 at.%) on both the solubility of hydrogen (and deuterium) and the rate of formation of the hydride (or deuteride). A long series of investigations (combined with published data) shows the following for V, Nb, and Ta:

1. For these three metals the heats of solution, H_s , of the hydride are in the range 0.10 eV to 0.15 eV. (i.e., about 2000 to 3000 cal is required to dissolve a mole of the metal-hydride in the metal). Likewise for the deuteride.
2. Dissolved oxygen greatly slows the rate of formation of the hydride (or deuteride).
3. Dissolved oxygen does not appear to affect the equilibrium solubility of hydrogen or deuterium. Thus the binding energy of H or D atoms to oxygen in a given metal must be less than H_s for that metal, but appreciably greater than zero.
4. H and D have the same solubility in Nb at low temperatures. Also in Ta.
5. For V, published results are in disagreement.
 - a. Oxygen does retard formation of hydrides or deuterides.
 - b. Heats of solution for both isotopes are in disagreement.
 - c. H and D may or may not have the same solubility at low temperatures.

The only serious remaining issue is thus for H and D in vanadium. D. Westlake at Argonne, T. Scott at Ames and I are the chief U. S. investigators whose results do not fully agree, probably because of the extraordinary importance of trace impurities. By exchange of specimens and by continued attention to impurities, we expect to resolve this issue.

The association with the Science Center at Rockwell International continues. Joint experiments on the elastic properties of Nb-H alloys with D. Thompson and Otto Buck are being carried out on a grant from NSF. Hydrogen produces large changes in the elastic constants of Nb, Ta and V. Changes for some of the fundamental constants are positive on hydrogen addition, for others negative. These results were interpreted to be a result of mechanical relaxation (i.e., rearrangements which lead to internal friction). We are attempting (1) to check the published results, (2) to see whether the changes in elastic constants may not be related to electronic effects rather than mechanical relaxations and (3) to measure the third order elastic constants to find the anharmonicity of the site in which the hydrogen sits.

Publications: (Calendar Year 1975)

Philippe Lecocq and Charles Wert
Equilibrium in Hydride Formation in Tantalum
Thin Solid Films 25, 77-84 (1975)

M.S. Theses: (Calendar Year 1975)

R. W. Levis (C. A. Wert, Adviser)
The Solubility of Hydrogen in Vanadium
August 1975

T. Wilken (C. A. Wert, Adviser)
The Morphological Structure Produced During Reduction of Blue Tungsten Oxide to Tungsten Metal
May 1975

Ph.D. Theses: (Calendar Year 1975)

None

ED-02-01-03-0 Physical PropertiesDielectric Solids

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

Supporting Agency: U. S. Energy Research and Development Administration

Senior Staff: David Payne, Assistant Professor

Junior Staff: Roberta M. Fay, Research Assistant
 Byung Ko, Research Assistant
 Sang Park, Graduate Student

Object: A new project was initiated in July, 1975 for the study of dielectric solids. Dielectric solids are a technologically important class of materials which are used in a variety of applications, including electrical insulation and transmission, capacitive components, energy storage and conversion, transducers, thermal controls and detection, imaging, displays, information storage and modulation. The project aims to contribute to a fuller fundamental understanding of structure-property relations by (1) preparing new highly polarizable materials, and (2) characterizing the dielectric behavior in both single crystal and polycrystalline form.

All crystalline solids may be classified according to their symmetry. Of the 32 crystal classes (point groups), 11 are centric and can not be polar. Of the remaining 21 acentric classes, 20 are piezoelectric (i.e. a mechanical stress induces electricity and conversely), and 10 have a unique polar axis along which they are spontaneously polarized. The value of the spontaneous polarization is dependent upon temperature, and if the temperature of the dielectric is altered, a change in polarization occurs which gives rise to a change in surface charge. This is known as the pyroelectric effect. If a component of the spontaneous polarization may be reversed by an applied electric field, this is known as the ferroelectric effect. Quartz is a well-known piezoelectric, but is not pyroelectric. The mineral tourmaline is highly pyroelectric (and therefore piezoelectric), but not ferroelectric, since electric breakdown occurs before polarization reversal. The synthetic compound BaTiO_3 is perhaps the best known ferroelectric (and therefore pyroelectric, and piezoelectric).

Concerning energy systems: piezoelectrics are used to transduce mechanical work into electric potential; pyroelectrics convert thermal changes into electric current; and ferroelectrics (which are highly susceptible to electric field changes) are used to store electric energy. We are searching for new and better materials and are currently investigating (i) piezoelectric Bi_2WO_6 and (ii) pyroelectric $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ which is also ferroelectric and optically active. In addition, the insulation reliability and dielectric strength of BaTiO_3 is being investigated with respect to stoichiometry, purity and structural order.

It is our belief that the study of single crystal dielectric materials will reach a level of understanding where an interpretation of the electric behavior of well-characterized polycrystalline systems should be possible in terms of modified single crystal properties. This investigation is concerned with this general problem and intends to explore the role of internal boundaries upon the dielectric behavior of ceramic systems. As such it is part of a larger program of research investigating the effects of ceramic microstructure upon the electrical characteristics of polycrystalline materials.

Results, FY 76:

Most Significant Accomplishments: The most significant accomplishment to date has been in the area of materials processing and fabrication studies. We have been successful in putting to immediate practical use the information generated from our synthesis studies on $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ and $\text{Pb}_5(\text{Ge},\text{Si})_3\text{O}_{11}$. This class of low melting point high dielectric constant ferroelectric materials is of considerable interest as a sintering aid for BaTiO_3 ceramics. Barium titanate based capacitors and transducers are normally fired between 1300 and 1400°C. By sintering in the presence of a liquid phase, rapid consolidation will occur through surface tension and capillary forces, if the liquid wets the solid particles. Dense diphasic BaTiO_3 - $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ ceramics have been successfully prepared by this technique of liquid phase sintering, at temperatures significantly lower than 1400°C and close to 750°C. This technical accomplishment means not only substantial energy savings will be realized in the electrical ceramics industry by reduced thermal processing, but also alleviates the dependence on expensive strategically important precious metals which are used as co-sinterable internal electrodes in integrated components.

Other Results: Lead germanate is trigonal (3) at room temperature, with a ferroelectric-paraelectric (3/m) transition at 177°C. The polar axis is along the C direction, and the phase transition may be moved towards room temperature by Si substitution. Experiments in this laboratory have verified that lead germanium silicate glasses may be formed and subsequently recrystallized. The dielectric properties of both sintered and recrystallized $\text{Pb}_5(\text{Ge},\text{Si})_3\text{O}_{11}$ compositions have been characterized and the phase transition behavior of lead germanium silicate appears to have a high degree of second order. Thin plate-like crystals grow from the glass, and in thin layers the polar axis is perpendicular to the sample surface. The implications are extremely encouraging for the fabrication of large surface area pyroelectric detectors by glass coating techniques. Besides thermal control devices, the possibility of efficient pyroelectric generators is conceivable at temperatures below the Debye temperature.

The growth of single crystal Bi_2WO_6 and Bi_2MoO_6 is being attempted. Initial experiments are underway by the hydrothermal method, flux growth, double decomposition, vapor transport and the gel method. Special crystal growth equipment has been designed. The system Bi_2O_3 - WO_3 has become of

considerable technological interest in recent years due in part to the discovery of new solid state materials suitable for a variety of improved energy applications, ranging from catalysis to galvanic energy cells and dielectric devices. Even though there appears to be some question concerning the number and types of stable phases present in this system, there is little doubt that the most refractory compound is bismuth tungstate (Bi_2WO_6), a compound which melts congruently at 1080°C . Large single crystals can be pulled from the stoichiometric melt, but unfortunately they crack on cooling, with polycrystallization of the boule being attributed to a destructive phase transformation at approximately 935°C . Consequently, little is known about the intrinsic properties of strain free single crystal Bi_2WO_6 . The room temperature crystal structure of Bi_2WO_6 is orthorhombic mm^2 . Tungsten is displaced $0.44 \text{ \AA}$ from the center of the oxygen octahedra along the polar axis; and assuming complete ionic bonding a theoretical spontaneous polarization value of $P_s = 0.42 \text{ c/m}^2$ can be calculated. This is nearly twice the value for BaTiO_3 and indicative of the potential use of Bi_2WO_6 in piezoelectric, pyroelectric, and possibly ferroelectric applications. Coupled with the high refractive index associated with dense highly polarizable structures, a definite possibility is apparent for property improvement in acoustooptic and electrooptic devices. Therefore, a need exists for the growth and evaluation of single crystal Bi_2WO_6 .

So far we have been able to recrystallize Bi_2WO_6 by the hydrothermal method at temperatures significantly lower than the polymorphic transition. Optical examination of 1 mm size crystals (recrystallized at 400°C) indicate the crystals were strain free and contained no apparent domains. X-ray results were in excellent agreement with previous data. Single domain crystals were placed in extinction in cross polarized light and heated on the hot-stage microscope. No phase transformation was observed at 935°C . With slow heating rates, optical transmission became apparent only at 900°C within localized volumes, and the crystals became completely transparent at 1010°C . On slow cooling, a phase transformation was not observed at 935°C , but rather at 860°C , and below this temperature the crystals were found to contain many domains. Hysteresis in the phase transformation was again observed on recycling the temperature, and this time the crystals catastrophically cracked at 1010°C . The fracture energy was sufficient to lift the crystals off the microscope stage and out of the field of view. It is interesting to note: the transformation observed at 860°C with decreasing temperature for hydrothermally grown single crystal Bi_2WO_6 , coincided with the previously observed temperature for crack initiation in Czochralski boules. Apparently, domain formation was insufficient for relieving transformation strain (resulting from the prototypic-polar transition), and elastic failure subsequently occurred. Strain free single domain Bi_2WO_6 crystals (1 mm) were grown by the hydrothermal method, at temperatures significantly below the polymorphic transformation. No doubt larger crystals (1 cm) may be grown in the future, similar to the developments made for α -quartz. This could give rise to some interesting electromechanical energy conversion devices.

Another aspect of our research activity has been concerned with thin-film and thin-layer capacitive devices. For example, Bi_2WO_6 can be sputtered onto substrates, and when annealed in air at 250°C the films are highly crystalline. Bismuth tungstate belongs to the bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) family of materials, of general formula $\text{Bi}_2\text{M}_{n-1}\text{R}_n\text{O}_{3n+3}$, which consist of Bi_2O_2 layers interleaved by $\text{M}_{n-1}\text{R}_n\text{O}_{3n+1}$ perovskite like layers. For Bi_2WO_6 , $n=1$; and if the layered structure deposits epitaxially with the polar vector normal to the substrate surface, this configuration would be extremely suited for acoustic delay line applications. We have also determined how to evaporate Bi_2O_3 insulating films, and are investigating the effect of Bi_2O_3 coatings on doped ZnO single crystals of various resistivities. Electrical measurements will contribute to our understanding of varistor behavior in complex polycrystalline heterogeneous ceramics which exhibit non-ohmic current-voltage characteristics similar to back-to-back Zener diodes. A model varistor system consists typically of a major dispersed phase of semiconducting ZnO grains which are isolated from each other by an intergranular phase of insulating Bi_2O_3 . The technical importance of these devices is that they may have greater power handling capabilities for voltage surge protection than Zener diodes. However, little is known about the nature of the intergranular phase which is property controlling. The research to date has been two-fold: (1) an investigation of the effects of systematic chemical substitutions within the boundary phase on electrical ceramic properties, (2) the fabrication of simple bi-crystal devices for dielectric dispersion measurements and Cole-Cole analysis. A better understanding of the role of intergranular impedance layers on electrical properties of ceramic devices should develop from this investigation.

Dielectrics for energy storage require high dielectric constants and electric strengths. Investigations are underway by which reliable dense fine grain dielectrics may be fabricated from high dielectric constant ferroelectric materials. The deleterious effect of processing contaminants (e.g. SiO_2 , Al_2O_3) on high power factors and low resistivities have been characterized, and verified by purposeful chemical additions. The effect of anion vacancies on long term electrochemical degradation of insulation resistance has been investigated further, and a method of predicting reliability from current voltage measurements has been extended to include proton and hydroxyl charge transport. The results on reliability assurance have been extremely successful, and industry today is using this technique for testing dielectric components which will be used under continuous electrification. Indeed, we have a test named after us!

Results Expected, FY 77: We plan to continue our work on crystal growth, synthesis, ceramic preparation and dielectric evaluation of $\text{Pb}_5(\text{Ge}_3\text{Si})_3\text{O}_{11}$, Bi_2WO_6 and associated derivative structures. The phase transition behavior of lead germanate will be characterized as a function of isomorphous chemical substitutions, particularly with Ca, Sr and Ba. We are searching

for a broad distributed "second-order" type phase transition which would be suited for improved pyroelectric thermal sensors and electric generators. One aspect of our work will be concerned with the recrystallization behavior of glass-ceramic layered coatings, (suitable for solar energy collectors), in an applied electric field. This technique would pole the crystals in a preferred alignment as they grow in the glass. As far as we are aware, this approach has never been attempted, and if successful, the single domain aligned polar crystals would maximize the pyroelectric efficiency. The pyroelectric effect is a 24-hour phenomenon, day after day, and unlike the photoelectric effect, independent of sunlight. A pyroelectric generator would work continuously (provided time dependent changes occurred--naturally or man made) at any location and latitude on earth or in space!

Hydrothermal crystal growth of Bi_2WO_6 will be continued in a larger 500 ml pressure vessel constructed out of HY 100 stress corrosion resistant steel. The use of baffles, extended growing times and higher pressures will be investigated. Ceramic specimens (fabricated by conventional sintering processes) will be poled and the piezoelectric properties determined. We plan to continue our interaction with the Coordinated Science Laboratory on sputtered Bi_2WO_6 thin films. The evaluation of new piezoelectric materials will be continued and crystal growth studies initiated for candidate materials like $\text{Ba}_2\text{TiSi}_2\text{O}_8$ and PbTiO_3 .

Dense diphasic dielectrics fabricated by the technique of liquid phase sintering in the system $\text{BaTiO}_3\text{-Pb}_5\text{Ge}_3\text{O}_{11}$ will be characterized further. Of particular interest is the energy storage capability at high electric fields. Diffusion couples, wetting studies, and mixture reactivity will be determined by XRD, EPMA, SEM and Curie-Weiss analysis. The effect of particle size distribution on wetting without crystalline substitution will be determined, and the high field properties measured. The concept and practice of electric field splitting by microstructural engineering is to be developed further.

Results Expected, FY 78: We expect to continue our work on crystal growth of polar materials and develop the capability of top-seeded flux pulling. The characterization technique of second harmonic generation (SHG) in acentric solids will be introduced for evaluation of new materials suitable for energy conversion applications. The novel technique of Curie-Weiss analysis will be developed further for determining reaction kinetics in ferroelectric mixtures by comparison with thermal SHG data. Curie-Weiss analysis is several orders of magnitude more sensitive than XRD. The ferroelectric behavior of polycrystalline NaNbO_3 (which in single crystal form is antiferroelectric) will be examined, and a thermodynamic analysis formulated to determine if anisotropic grain boundary thermal stress is sufficient to modify the properties of the polarizable deformable solid. The electric and dielectric nature of grain and phase boundaries in electrical ceramics will be investigated further. We plan to use Auger spectrometry to determine depletion layer depths at interfaces in varistors and thermistors, and correlate this information with calculated values from impedance measurements. The purpose of this work is to obtain a more fundamental understanding of the role of microstructure upon electrical properties and develop the concept of microstructural engineering for property optimization in energy related materials.

Relationship to Other Federally Funded Projects: The crystal growth and characterization studies are related to other materials research projects in this Laboratory. In addition, the determination of structure-property relations in single crystals, and texture effects in polycrystalline systems are of importance to the program in Materials Engineering. Our findings on new piezoelectric and ferroelectric solids are of practical significance to the acoustic delay line project in the Coordinated Science Laboratory and the acoustooptic--electrooptic effort on quantum electronics in Electrical Engineering. New pyroelectric materials are of considerable interest to members of the Ceramic Engineering faculty concerned with Ceramics for solar energy. Also, the melting points of highly polarizable $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ (750°C) and Bi_2WO_6 (1080°C) are of practical importance to the program on liquid phase sintering of diphasic dielectric mixtures (funded by the National Science Foundation) in the Department of Ceramic Engineering. The theoretical and experimental studies on the effects of polycrystalline microstructure on dielectric properties relate to other electrical-ceramic programs which are concerned with the role of interfacial impedance layers on the properties of semiconducting ferroelectric thermal sensors and current limiters, and $\text{ZnO}/\text{Bi}_2\text{O}_3$ voltage overload protection devices which are now being considered for application in high power transmission equipment.

Publications: (Calendar Year 1975)

None

M.S. Theses: (Calendar Year 1975)

None

Ph.D. Theses: (Calendar Year 1975)

None

Nuclear Magnetic Resonance Studies of Metals and Polymers

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

Supporting Agency: U. S. Energy Research and Development Administration

Senior Staff: Theodore J. Rowland, Professor

Junior Staff: Lance C. Labun, Research Assistant
Patrick Lenahan, Research Assistant
Robert S. Shalvoy, Research Assistant

Object: This program has applied nuclear magnetic resonance techniques to the study of metals and polymers. The central theme is the investigation of local electric and magnetic field configurations within metallic crystal lattices. These fields reflect the effect of atomic size and valence on alloy properties and the manner in which local electron densities respond to the introduction of impurities into the crystal lattice. The capabilities of NMR for the measurement of atomic mobility are applied to the determination of the diffusion coefficients and motional correlation times in solids.

Since metallic systems remain the predominant materials for mechanical and structural use, their investigation will continue to be stressed. Future energy conversion devices will operate at high temperature for thermodynamic reasons and in complex environments which will introduce foreign, usually deleterious materials. Solute interactions and atomic diffusion will be of crucial importance and nuclear magnetic resonance is a powerful technique for their investigation.

Diffusionless phase transformations influence the phonon spectrum of certain alloys at temperatures far higher than that at which the low temperature phase is stable. These structural fluctuations deserve intense scrutiny because they undoubtedly play a role in high temperature atomic migration. They have been identified in just those alloys (Ti, Zr, Hf-V, Ta, Cr, Mo, W) which appear promising on other grounds for advanced design applications. Present experimental data has suggested the nature of these heterophase fluctuations but the local symmetry is still to be determined and, most importantly, the lifetime of the fluctuations is unknown. These quantities are critical for the determination of the full utility of this unusual behavior. Since nuclear resonance techniques are ideally suited for their study, their exploration is a significant goal of the program.

Recent and ongoing investigations include the investigation of interstitial transition metal solutes and oxygen and nitrogen in vanadium. Since the vanadium nuclear magnetic resonance is particularly sensitive to these interstitial impurities, it was desirable to understand their effect

thoroughly before proceeding with the analysis of other alloys. Data for the solutes Ti, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, W, and Pt in V indicate that solute screening is of short range and less significant than the size of the solute as measured by its effect on the V lattice parameter.

Studies of Group 8 transition metals in copper and of concentrated alloys of Group B elements with copper have greatly extended our knowledge of metallic solid solutions. Related systems studied have included aluminum, aluminum alloys, the intermetallic compounds V_3Si and V_3Ga , and the age hardening of Cu-2 wt% Be alloys. The interpretation of the latter experiments relied on an earlier investigation of Cu-4.8 at.% Ag alloys. The studies of atomic motion have been extended, recently, to include the diffusion of H in Nb, the effects of hydrogen bonding in liquid amines, and molecular motion in three-dimensional organic networks of crosslinked polybutadiene. The central theme of the research remains, however, the electronic structure of metals and their alloys and its effect on atomic motion and structural properties.

Results, FY 76:

Most Significant Accomplishments: The completion of the study of age hardening in copper-beryllium alloys revealed general coherent precipitation of the compound CuBe on a scale so fine as to have escaped detection by electron microscopy.

Other Results: The experimental phase of an investigation of the relationship between nuclear relaxation and the average network chain length in polymers was completed. The significance of the results lies in the characterization of the restricted chain motion and the application to curing phenomena in certain thermosetting materials.

An initial series of measurements of proton relaxation in Nb-2 at.% H alloys from -100°C to 45°C has been completed. These results are a contribution to the group study of hydrogen in metals at Illinois and a preparation for our projected investigation of phase stability in transition metal alloys.

Results Expected, FY 77: The investigation of diffusion of hydrogen in Nb and in other transition metal alloys will continue in cooperation with H. Birnbaum and collaborators. The effect of other interstitial solutes on trapping of hydrogen will be determined.

Heterophase fluctuations in ω phase alloys like Zr-Nb and Ti-V will be pursued with the specific objectives dependent on the results gained from present initiatory experiments. Our experience with these nuclei indicates that such experiments will detect changes in the local atomic symmetry accompanying the phase fluctuations, and also reveal the average time interval during which the metastable phase exists. In the course of these experiments the Knight shift and ordinary (static) quadrupole effects will be monitored as a function of temperature.

The structural transformations we propose to investigate utilize several of the well-known interactions between the lattice electrons and the nuclei. Evidence from neutron scattering and X-ray diffraction experiments indicate the presence of quasi-static thermal excitations existing in the alloys which exhibit the ω -phase transformations. The fluctuations, even at temperatures many hundreds of degrees higher than the athermal ω -phase transformation, appear to exist for times long relative to the lattice vibrational period. Since the transition involves a displacement of lattice planes in the original bcc structure, there will exist charge density shifts stabilizing the new structure. These fluctuations are rapid, and large compared to ordinary atomic lattice vibration amplitudes. Their practical significance lies in their effect upon the mechanical and annealing properties of these alloys at elevated temperatures.

Work initiated in the area of crosslinked polymers will have been completed, and its future is at present uncertain. The results can be expressed briefly in terms of the extent to which chain motion is inhibited by crosslinking. Relaxation measurements of the type conducted essentially single out specific frequency components of molecular motion. This study, if continued, will be specifically aimed at determining the spectral distribution of the motions in crosslinked polybutadiene and in certain block copolymers of polybutadiene. Motion is highly correlated in these materials and there is no single statistically independent motional time or even distribution of such times which can characterize the molecular motion. Further productive work in this area may require more support than can presently be spared from other aspects of this program, and the work will be discontinued if equipment capable of relaxation measurements over a wide frequency range cannot be obtained. It was planned to devote no more than one third of the total program effort to this pursuit in any case.

Results Expected, FY 78: The focus will continue to be the understanding of the mechanism by which elements propagate the effects of their valence and size difference through the metallic lattice. This has been the central theme of this work for an extended period, but now it appears that the emphasis must shift to elevated temperature studies of transition metals and their alloys, and concomitantly to the effect of interstitial additions to these systems. There are many similarities among related transition metal systems, reminiscent of well-known valence effects in the Group A metals; efforts to maximize the significance of our experiments will exploit these relationships. The overwhelming proportion of our past work has involved the study of charge density in alloys via nuclear-electron interactions. This is the dominant theme about which the program coheres. The ramifications of such information are widespread, and basic to the evolution of alloys.

We have for many years followed with interest and appreciation the work of P. Beck. Our close contact and continuing discussions of his work on the conditions for the existence of localized magnetic moments in alloys of non-magnetic with magnetic elements have suggested nuclear resonance experiments which would complement his studies. The measurements of

Beck's group are macroscopic in nature, consisting primarily of observations of susceptibility and magnetization, by both ac and dc techniques. The interpretation usually rests upon the existence of certain atomic configurations. The latter, when treated self-consistently, lead to the observed property. There is no serious doubt of the validity of Beck's analyses, yet frequently it would be satisfying if experiments which are essentially atomistic in nature were conducted in a collaborative fashion. We believe such work could lead to fruitful new insights into the nature of the interactions involved, and in view of the role of magnetism and magnetic properties in many aspects of energy conversion we conceive this work as lying within the scope of the present program.

Relationship to Other Federally Funded Projects: The strength of the research program of the College of Engineering at the University of Illinois in the areas of diffusion, defect structure, phase transformations, radiation damage and electronic structure provides an essential environment for the present and proposed work. The research is influenced by and cooperates with the overall thrust on hydrogen in metals of H. Birnbaum and collaborators, with studies of interstitial solid solutions of C. Altstetter and C. Wert, with P. Beck's investigation of the magnetic properties of transition metal alloys, and the NMR research of C. Slichter. The research on amorphous polymers has benefited greatly through close association with the theoretical work of R. Gaylord and with the high pressure polymer research of J. Jonas.

The objectives of the program are closely related to those of groups at Argonne National Laboratory and the Ames Laboratory with whom effective contact is maintained.

Publications: (Calendar Year 1975)

T. J. Rowland

A ^{14}N Nuclear Relaxation Study of Hydrogen Bonding in Diethylamine-Alcohol Solutions

J. Chem. Phys. 63, 608-612 (1975)

T. J. Rowland and A. C. Yen

A Study of Precipitation Using Nuclear Magnetic Resonance: Cu-2 wt.% Be
Acta Metall. (in press)

M.S. Theses: (Calendar Year 1975)

None

Ph.D. Theses: (Calendar Year 1975)

None

ED-02-02-00-0 SOLID STATE PHYSICS SUMMARY

The solid state physics research can be divided into the two broad areas of (1) research on the electronic structure of materials of importance for the understanding and control of the flow, conversion and storage of energy and (2) research on the aspects of crystal structure and its defects which are basic for an understanding of mechanical and thermal properties.

Application of high pressure to solids, ranging to hundreds of kilobars, decreases the atomic spacing with a resultant perturbation of the electronic structure. Professor H. Drickamer has exploited this technique to quantitatively characterize electronic transfer processes in alkali halides, demonstrate that protein denaturation occurs in steps that can be reversible, make a critical test of Mulliken's theory of charge transfer complexes, discover hydrocarbon dimers and tetramers of novel structure and demonstrate the transition from photochromism to piezochromism with pressure. The observations on protein denaturation will be quantified during the next year and the study of energy transfer in phosphors extended in conjunction with research on organic photochemistry and photoconductivity in zinc sulfide and silicon.

The magnetic properties of transition elements in non-magnetic host metals have been investigated by Professor C. Slichter who has determined the position of the energy levels, the crystal splittings of the 3d electrons, and the number of d electrons of iron in copper through nuclear magnetic resonance measurements. These measurements are being extended to Co, Cr, and Mn in copper where the data have proven the importance of crystal

splitting for the magnetic properties of iron group atoms in metals. The resonance technique will be applied to the electronic structure of layer compounds like TaSe_2 with a test of Professor W. McMillan's theory of incommensurate charge density waves. Another area of application of the resonance technique that will be continued is the electronic structure of commercial hydrocarbon catalysts of platinum on silica and alumina substrates.

A new project of Professor J. Dow will investigate theoretically the electronic processes that determine the absorption and emission of electromagnetic radiation by real solids. Problems to be investigated are two photon absorption, field ionization of excitons, the effect of internal fields due to impurities and phonons in limiting transparency of the optics of laser systems. This research is pertinent to photovoltaic and photothermal energy conversion, thermoelectric effects, and the use of synchrotron radiation for the study of surfaces, impurities and defects.

A second new experimental program, carried out by Professor D. Ginsberg, in cooperation with the group studying gases in metals is the effect of hydrogen on the properties of superconductors. The focus of immediate interest is the mechanism by which hydrogen can increase the transition temperature of niobium, the increase of energy losses in niobium superconducting accelerators, and the production by hydrogen of superconductivity in metals like platinum. The results are expected, however, to contribute broadly to the understanding of the effect of hydrogen on the properties of the refractory metals.

The effect of crystalline defects on the mechanical and thermal properties of solids has been an area of traditional strength at Illinois with major contributions from Professors A. Granato, D. Lazarus, J. Koehler and R. Simmons.

The ultrasonic techniques of Professor A. Granato are applied to the study of interstitials in metals, dislocations and the strength of metals, and non-linear elastic behavior. These experiments have recently extended the theory of the effect of dislocations on internal friction and provided a synthesis of theories of mechanical behavior of crystals. In the immediate future, experiments will concentrate on the structure of interstitials in metals and hydrogen in palladium, on the development of the theory of dislocation interaction with obstacles and a test of the temperature dependence of the elastic constants of ionic crystals and metallic alloys.

The diffusion studies of Professor D. Lazarus are concentrated on the diffusion mechanisms that exist in the anomalous bcc transition metals, like titanium, and the superionic conductors, like RbAg_4I_5 . Both classes of material show abnormal and extraordinarily large diffusion coefficients. A small negative activation volume has been found in RbAg_4I_5 so that interstitial silver atoms are probably the mobile elements. Future research will continue the investigation of superionic conductivity mechanisms which are of importance for the application of these materials in energy storage devices, complete the isotope diffusion measurements on titanium, and, because of its technological importance, test the feasibility of a basic investigation of wear and attrition of solid surfaces.

Professor J. Koehler's experiments on radiation damage and its annealing are now turning to the hexagonal and body centered cubic metals where little information is available. At issue are the properties of point defects, defect clusters, voids and the mechanisms of their formation and removal. It has recently been shown by Koehler that there are two classes of bcc metals with respect to the annealing of radiation induced defects. One class, of which iron and niobium are examples, shows a relatively high temperature Stage I annealing near 80 K; the other class shows low temperature Stage I annealing near 25 K. Presumably the interstitial structures, interstitial trapping, and void formation are different for the two classes. Electron irradiation experiments are planned on the hexagonal metals Mg and Cd and the bcc metals V and Cr. Inhibition of void formation through interstitial trapping by small core impurities will also be tested.

A remarkable result of Professor R. Simmons' measurements of the formation energy of thermal vacancies in bcc ^3He is that thermal motion occurs by quantum mechanical tunneling and that the defects have a non-localized structure with the properties of vacancy waves. This achievement is a major advance in our understanding of defect diffusion and the structure of quantum solids. The examination of thermal vacancies in ^3He - ^4He crystals is planned to determine the effect of isotopic mass and different statistics. Since tunneling has been verified as the migration mechanism for vacancies in bcc ^3He , the studies will be expanded to include hcp ^3He . Consideration is being given to the application of the sophisticated x-ray scattering techniques to charge density waves in layered compounds.

The superlattice period is short, diffuse scattering is large, and the problem is a difficult one.

The program of Professor A. Anderson which will be initiated during the coming year will use low temperature techniques to investigate the relationship between structural defects, interfaces and thermal energy transfer. Anderson has shown that thermal transport in glasses, ceramics and polymers is entirely by phonons (i.e., that the phonon concept is applicable to amorphous materials), that the extra specific heat of amorphous materials is due to localized excitations and that phonon scattering at the interface between amorphous materials is specular. His specific heat data on hydrogen in niobium has been used by Birnbaum and Flynn to verify their elegant theory of tunneling of interstitial hydrogen in niobium.

The planned research includes an investigation of the influence of grain boundaries on thermal conductivity where present theory and experiment differ by a factor of 10^4 , an investigation of the technologically important problem of heat transfer from solids to liquid helium and hydrogen, studies of the excitation spectrum of conducting ions in the superionic beta alumina and the development of apparatus for thermal expansion measurements with a resolution of 10^{-3} Å, a factor of 100 better than presently available. The dilatometer will be useful for studies of interstitial hydrogen in refractory metals, the excitation spectrum of ions in superionics, and the localized excitations of disordered materials.

ED-02-02-0 Experimental ResearchUse of Very High Pressure to Investigate the Structure of Matter

Principal Investigator: Harry G. Drickamer, Ph.D.
 Professor of Chemical Engineering and
 Physical Chemistry
 Member, Center for Advanced Study

Supporting Agency: U. S. Energy Research and Development Administration

Senior Staff: Harry G. Drickamer, Professor
 Kimihiko Hara, Research Associate (Begin 4/1/76)

Junior Staff: Kevin W. Bieg, Research Assistant and GE Fellow
 Eric N. Hockert, Research Assistant and AMOCO Fellow
 John W. Hook III, Research Assistant
 Gary L. House, Research Assistant and Union Carbide Fellow
 Dean J. Mitchell, Research Assistant
 William D. Drotning, Research Assistant (Term 10/15/75)
 Martin I. Finston, Research Assistant
 David I. Klick, Research Assistant
 Craig E. Tyner, NSF Fellow

Object: The fundamental thesis of our research program is that very high pressure is a most powerful, indeed an essential, variable for understanding electronic structure and electronic behavior in condensed systems. The central feature of this research has been the selection of those classes of materials and types of measurements which yield the most important information and most useful generalizations 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.

We list here a few items in each category which sample some past contributions in each of these areas. Below we discuss current and projected work which falls largely under categories (A) and (B). A reading of these sections is intended to convey the flavor and philosophy of the work without being an exhaustive list.

A. Characterization of Electronic States

1. Shifts of the absorption edge in insulators and semiconductors illustrate the expected reduction in energy gap in simple materials, as well as detailed information about the more complex structure of the conduction bands in silicon, germanium and related III-V, II-VI, and I-VII compounds.

2. Changes in the location and shape of optical absorption and fluorescence peaks with pressure have provided essential information about localized transitions. It has been possible to evaluate in detail a variety of characteristic parameters for configuration coordinate diagrams, as well as to improve our understanding of Jahn-Teller effects and photostimulated luminescence.

3. Mössbauer resonance studies of the change in isomer shift and quadrupole splitting with pressure have added considerably to our understanding of ionic and covalent bonding in ferrous and ferric compounds, especially organometallic materials. Measurements on bcc, fcc, and hcp transition metals have illustrated differences in the band structure of the bcc and close packed metals.

4. Mössbauer resonance studies of the magnetic field as a function of pressure have been helpful in understanding magnetism in iron, cobalt, and nickel, in palladium-iron and palladium-cobalt alloys, in a series of orthoferrites, and in Fe_3O_4 .

B. Critical Tests of Theories

1. Some of the earliest and most basic tests of ligand field theory as applied to transition metal complexes were obtained from high pressure optical studies. The measured changes in ligand field strength and interelectronic repulsion (Racah) parameters clearly illustrate the possibilities and limitations of the theory.

2. Our measurements of shifts of absorption edges combined with electrical resistance work constituted the first critical test of the approach to the metallic state as described by simple band theory.

3. Our studies of calcium and strontium listed under (C)-1 below provided a direct test of band structure calculations on alkaline earth and related elements.

4. Our studies on the shifts of electron donor-acceptor transitions with pressure formed a critical test of Mulliken's theory of charge transfer complexes.

C. Electronic Transitions

1. Resistance anomalies associated with electronic transitions have been observed in alkali, rare earth, and alkaline earth metals. In addition to the $6s \rightarrow 5d$ transition observed by Bridgman in cesium at 40 kilobars, there is a second resistance anomaly at 100 to 130 kilobars, possibly involving the $4f$ band. The $(n+1)s \rightarrow nd$ transition has been observed in rubidium and apparently in potassium. A number of resistance anomalies are observed in rare earth metals, probably associated with $4f \rightarrow 5d$ transitions. Calcium, strontium and ytterbium exhibit metal to semiconductor transitions associated with a simplifying of the shape of the Fermi surface with respect to the Brillouin zone boundary.

2. Insulator-metal transitions with a variety of characteristics have been observed. Transitions with no discontinuities in structure or resistance occur in iodine, in several crystals involving large organic molecules like pentacene, and in the thallous halides. Transitions involving discontinuities in resistance and changes in structure occur in silicon, germanium, and many III-V and II-VI compounds.

3. An extensive series of studies involving both Mössbauer resonance and optical absorption has revealed a rich variety of electronic transitions in iron compounds. These include both (reversible) high spin to low spin and low spin to high spin transitions which depend on the nature of the ligand and its binding to the iron. The reversible reduction of $Fe(III)$ to $Fe(II)$ has been observed in a wide variety of compounds. Optical studies have also demonstrated the reversible reduction of $Cu(II)$ to $Cu(I)$ as well as changes of oxidation state of $Sb(III)$ and $Sb(V)$ in mixed valence compounds. Intensive collaboration with C. P. Slichter, Professor of Physics, has resulted in considerable progress in explaining these and other electronic transitions.

4. A large decrease in $\pi-\pi^*$ excitation energy with pressure has been observed in many organic molecules. In some cases this is sufficient to permit thermal occupation of the π^* state at high pressure and consequent chemical reactivity of a new sort. Similarly the decrease in donor-acceptor excitation energy with pressure in a large variety of charge transfer complexes results in thermal occupation of the excited state and a series of new reactions. A detailed study of the behavior of iodine-pyrene and iodine-perylene complexes has demonstrated the existence of hydrocarbon dimers and tetramers with structures entirely unlike any previously reported.

5. In photochromic compounds an optically excited electron decays to a new metastable ground state which involves a change of chemical conformation. High pressure studies on bianthrone, spiropyran and anils demonstrate that pressure can change the relative energies of the stable and metastable state sufficiently to permit thermal occupation of the metastable state, i.e., piezochromism replaces photochromism at high pressure.

Results, FY 76:

Most Significant Accomplishments: (1) We have perfected a high pressure luminescence apparatus for pressures to 150 kilobars and have made a detailed study of impurity ions especially Tl^+ , In^+ , and Ga^+ in alkali halides. From peak shifts and shape changes with pressure we have evaluated the configuration coordinate parameters (displacement and force constants of the electron ground and excited states). We have demonstrated that the relative intensity of the Jahn-Teller split component of the spectrum is distinctly pressure dependent and that therefore these components couple significantly to the totally symmetric vibrational coordinate. We have measured the rates of the electron transfer processes $In^+ + V + h\nu \rightarrow In^{++} + F$ and $In^{++} + F + h\nu' \rightarrow In^+ + V$ (where V = vacancy and F = color center) as a function of pressure and have demonstrated that the effect of pressure can be predicted quantitatively from measured overlap integrals. These studies constitute the most detailed and quantitative characterization ever done on these processes in the alkali halides and will be presented in a set of four papers in the June 15 Physical Review.

(2) In collaboration with G. Weber, Professor of Biochemistry and Biophysics, we have developed a technique for studying protein denaturation under pressure by means of fluorescence. Protein is the major source of energy for living creatures, and the denaturation process is poorly understood. We have been able to demonstrate that the changes of conformation take place in steps, e.g., the tryptophans quench between 3 and 6 kilobars while the positive charges become available for complexing in the range 6 to 12 kilobars. We have shown that only a fraction of the total possible sites actually change conformation in the denaturation process, that the volume change associated with each step is less than 1% of the molar volume, and that the process can be reversible. These studies are in their early stages, and only one protein has been studied quantitatively, but the technique shows great promise.

Other Results: (1) Our initial work concerning pressure effects on energy transfer in phosphors indicates that high pressure studies are providing a quantitative test of Forster-Dexter theory. The importance of this work and our future plans are discussed below. (See FY 77)

(2) We have developed a technique to measure the effect of pressure on phosphor decay rates as fast as 0.1 microsecond. We plan to apply this technique to a wide variety of phosphors.

(3) We have shown that there is a very large effect of pressure on the quantum efficiency of phosphors. For localized excitations in oxygen dominated phosphors this can be explained in terms of changes in the configuration coordinate parameters which can be calculated from peak shifts. Thus one can predict phosphor efficiency from peak shift data. For doped ZnS and ZnSe phosphors the efficiency depends on movement of trapping levels which we can determine with our new high pressure thermoluminescence apparatus. These phosphors have great importance in practical devices such as fluorescent lighting and oscilloscope screens.

(4) We have initiated a rather extensive program of high pressure organic photochemistry. A considerable fraction of this program is a joint effort with Gary Schuster, a very bright young Assistant Professor of Organic Chemistry. It has been demonstrated that excited triplet states increase in energy with pressure relative to excited singlet states; occupied nonbonding levels increase in energy relative to bonding levels. Many organic photochemical reactions proceed only when one of these states is preferentially occupied. The effect of pressure on the reaction yields and rates provides a clear-cut test of mechanism.

Many photochemical reactions are of great practical importance but are poorly understood--an example is photosynthesis, a second is the operation of the eye, and a third is photopolymerization. We believe our experiments may contribute significantly to the necessary understanding.

Results Expected, FY 77: Our plans for 1977 can be divided into two categories: extension and completion of current work and the initiation of new projects.

(A) 1. We plan to extend and to quantify our studies of protein denaturation. In particular, we hope to classify more accurately the types of sites which denature in different pressure ranges in different proteins and the fraction of sites of each kind which are involved in the process.

2. We plan to extend greatly our study of energy transfer in phosphors--to organic crystals, to plastic media, and to liquid solutions. Energy transfer is an essential step in many practical processes from fluorescent lighting to photosynthesis, and its complete understanding is essential. Our measurements of decay rates are basic to this understanding.

3. We plan to complete our studies of quantum efficiency of inorganic phosphors, to show the possibilities of present theory, and to develop refinements of the theory. Again, a study of decay rates is essential as well as high pressure thermoluminescence measurements.

4. We plan to extend greatly our work on organic photochemistry. Our initial work shows very large effects on photochromic processes, on reaction rates of aryl ketones, and on a variety of other reactions, as well as on fluorescent and phosphorescent yields. This area appears to be one of the most promising for future development.

(B) 1. We have tested the feasibility of high pressure photoconducting and photovoltaic effects. We have designed an apparatus and plan to initiate studies on CdS and selenium with a variety of dopants. We will ultimately extend our work to silicon, to ZnS, and to organic photoconductors. A better understanding of photoconductivity is very relevant to aspects of the solar energy problem.

2. We have designed an apparatus for measuring the depolarization of molecules by pressure. It should be particularly effective for studying macromolecules in solution. Depolarization of light is a very effective way of characterizing change of conformation of a large molecule. It is also an essential feature of many photochemical processes.

Results Expected, FY 78: Our plans for 1978 envision an extension of our present work and expansion into new areas where we can use pressure to increase our understanding of electronic processes in condensed systems. We believe that various aspects of organic and inorganic photochemistry and photoconductivity have so many facets and such wide applicability in improving energy conservation that we will be concerned with these processes for a considerable period to come.

As outlined in Object, our theme is the essential nature of pressure for understanding electronic behavior. We continue to develop various aspects of this theme to fill out the three categories of phenomena we discussed in that section. In a real sense this is a continuing program. We try to exploit given techniques and study given classes of materials long enough to establish generalizations which form the basis for new theory, or the critical test of existing theory, without, however, becoming a factory to crank out data. The program is an evolving one as new techniques are introduced to study new aspects of science or new materials and as we discover new phenomena around which to reorient our research.

Relationship to Other Federally Funded Projects: There is really no other laboratory in the world which duplicates any significant fraction of our studies on pressure and electronic structure. McWhan and Jayaraman at Bell Labs have made significant contributions 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 project.

Our expertise contributes in an indirect way to a continuing interaction with the Catalyst Group at the Corporate Research Labs. of Exxon Research and Engineering.

2

Publications: (Calendar Year 1975)

H. G. Drickamer

The Effect of Pressure on the Electronic States of Organic Solids
Proceedings of International Conference on Organic Synthesis, Belgium, 1974.
 Pure and Applied Chem. 43, 379-399 (1975)

H. G. Drickamer

Exploratory Research at High Pressure
Materials Under Pressure, edited by T. Hirone (Maruzen Press Co., Tokyo, 1975),
 pp. 1-35

H. G. Drickamer

High Pressure Studies of Electronic Structure in Solids
International Review of Science - Inorganic Chemistry, Vol. 10, Solid
 State Chemistry, edited by L. E. J. Roberts (Butterworths, London, 1975), pp. 1-33

D. G. Wilson and H. G. Drickamer

High Pressure Studies on Spiroprans
 J. Chem. Phys. 63, 3649-3655 (1975)

W. D. Drotning and H. G. Drickamer

High Pressure Optical Studies of Doped Alkali Halides. I. Peak Shifts and
 Peak Shape Changes
 Phys. Rev. (in press)

W. D. Drotning and H. G. Drickamer

High Pressure Optical Studies of Doped Alkali Halides. II. Jahn Teller Effects
 Phys. Rev. (in press)

W. D. Drotning and H. G. Drickamer

High Pressure Optical Studies of Doped Alkali Halides. III. Rates of Electron
 Transfer Processes
 Phys. Rev. (in press)

W. D. Drotning and H. G. Drickamer

High Pressure Optical Studies of Doped Alkali Halides. IV. Mixed Crystals
 Phys. Rev. (in press)

C. E. Tyner, W. D. Drotning, and H. G. Drickamer

Asymmetric Line Shapes of Localized Optical Excitations in Condensed Systems
 J. Appl. Phys. (accepted)

M.S. Theses: (Calendar Year 1975)

E. N. Hockert (H. G. Drickamer, Adviser)

The Effect of Pressure on the Electronic Spectra of Some Salicylikineaniline
 May 1975

G. L. House (H. G. Drickamer, Adviser)
Effects of High Pressure on the Luminescence of Zinc Sulfide Phosphors
May 1975

C. E. Tyner (H. G. Drickamer, Adviser)
Effects of Pressure on Oxygen Dominated Phosphors
May 1975

Ph.D. Theses: (Calendar Year 1975)

W. D. Drotning (H. G. Drickamer, Adviser)
Luminescence of Impurity-Activated Alkali Halides Under High Pressure,
Vols. I and II
October 1975

D. G. Wilson (H. G. Drickamer, Adviser)
Photochromic Studies of Spiropyrans
May 1975

Anharmonic Effect in Solids

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

Supporting Agency: U. S. Energy Research and Development Administration

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

Junior Staff: Terrell D. Berker, Research Assistant
Randall D. Isaac, Research Assistant and Fellow
David L. Johnson, Research Assistant
David B. Poker, Research Assistant and Fellow

Object: This research program uses the unique capabilities of ultra-sensitive ultrasonic techniques to investigate the structure of interstitial atoms in metals (including hydrogen in metals), to determine the role of dislocations in determining the strength of metals, and measure non-linear elastic properties which determine the thermal behavior of solids. The phenomena under investigation are all of central importance for the use of metal structures under extreme conditions of temperature, stress, and hostile environments which induce contamination by foreign impurities.

The attenuation and velocity of ultrasonic waves are measured to obtain the mechanical response of perfect and nearly perfect crystals to applied forces. Especial use is made of techniques with a sensitivity of as much as one part in 10^7 for elastic constant changes. Specific objectives of this program are:

A. Interstitials in Metals. We are studying the structure of point defects produced during radiation and annealing of metals. The structure is deduced from the anisotropy, relaxation and resonance type behavior of elastic constant changes produced by radiation damage. The information is basic to the understanding of how defects combine to produce larger agglomerates. The same techniques are being used for the study of the structure of hydrogen in metals.

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

C. . Non-linear Elastic Effects. Many thermal properties of solids depend upon deviations from linear elastic behavior. We are measuring the temperature dependence of elastic constants at low temperatures where the elastic constant changes can be used to determine third and fourth order elastic constants. This data is of use in determining useful empirical interatomic potentials and equations of state.

Results, FY 76:

Most Significant Accomplishments: (1) We have extended the theory of amplitude independent internal friction by dislocations in two ways. The first way allows for long-range pinning by dipolar point defects and gives an expression for the pinning force in terms of the concentration of defects. The second way permits one to determine separately the changes in viscous drag and pinning drag forces. This second result was used to demonstrate that the changes observed by Simpson and Sosin during irradiation (peaking effect) are in general due to both a pinning and drag, and not solely due to a drag as had been previously supposed. The first result was used to demonstrate that pinning observed in neutron irradiated copper at 20 K is due to long range pinning from isolated interstitials, and not from short range pinning from lattice effects as had been assumed. The analysis demonstrates that such pinning effects can be used to detect interstitials in concentrations as small as one part in 10^7 .

(2) We have begun a synthesis of theories of mechanical behavior of crystals which embraces macroscopic (stress-strain, creep, recovery) and microscopic measurements (internal friction). This involves classification of forces into viscous, inertial, and restoring types, represented by mechanical models. The forces are further classified according to whether they are linear or non-linear, short range or long range and small, moderate or large. The synthesis relates many effects previously thought to be unrelated. A preliminary account of this work was given at the Gatlinburg Conference on Radiation Damage.

Other Results: The breakaway stress for dislocations in copper with small concentrations of aluminum has been found to have a maximum as a function of temperature. This is believed to be the result of inertial effects operating at temperatures as high as 50 K. Such behavior is consistent with results found earlier for superconductors within the framework of our inertial model for the strength of crystals. Work is continuing on this project. The significance of the result is that it suggests that the traditional theories of strength may be not generally valid at low temperatures.

Results Expected, FY 77: (A) More systematic and detailed measurements of the effects of close pairs and free interstitials separately in copper will be made. Also, measurements are in preparation for the resonance behavior of "mixed dumbbells" (interstitials combined with an impurity) in aluminum. Measurements of elastic constant changes of Pd containing

hydrogen have been made and measurements with deuterium are in progress. A He^3 refrigerator will be constructed for the detection of resonance mode effects at low temperatures.

(B) Breakaway stresses in lead in both the superconducting state and at temperatures above the superconducting transition temperature are in progress. Changes in attenuation at 10 MHz are being measured simultaneously with breakaway stresses at 10 kHz in an effort to further test predictions of the inertial model of dislocation interactions with obstacles.

(C) Measurements of elastic constant changes as a function of temperature in the low temperature T^4 region are being made in LiF, beta brass and RbMnF_3 . These results will be analyzed in terms of nearest and next-nearest neighbor interactions to determine suitable interatomic potentials for these substances, and to test a theory for the temperature dependence of elastic constants.

Results Expected, FY 78: We are expanding our efforts in the direction of more detailed studies of the effects of dipolar point defects on the mechanical properties of solids. It is intended that the basic properties (symmetry, relaxation, and resonance modes) of such defects will first be studied. This should be followed by studies of the effects of such defects on the mobility of dislocations.

Relationship to Other Federally Funded Projects: We are cooperating with Jon Holder of MRL in studies of radiation damage in metals and the theory of deformation of ice crystals. A seminar on properties of crystals containing dipolar point defects is in progress combining students from our group with those of J. Holder and J. Koehler. The work on hydrogen involves consultations and cooperation with many others in MRL participating in the hydrogen in metals thrust.

Publications: (Calendar Year 1975)

J. A. Garber and A. V. Granato
Fourth-Order Elastic Constants and the Temperature Dependence of Second-Order Elastic Constants in Cubic Materials
Phys. Rev. B11, 3998-4007 (1975)

J. A. Garber and A. V. Granato
Theory of the Temperature Dependence of Second-Order Elastic Constants in Cubic Materials
Phys. Rev. B11, 3990-3997 (1975)

A. V. Granato
Ultrasonic Studies of Mechanical Strength
Ultrasonics Symposium Proceedings, IEEE Cat. #75 CHO 994-4SU (1975)
Also supported by NSF

R. D. Isaac and R. B. Schwarz
A Simple Persistent Switch for Superconducting Solenoids
Rev. Sci. Instrum. 46, 638 (1975)

K. D. Swartz, W. Bensch, and A. V. Granato
The Second-, Third-, and Fourth-Order Elastic Constants of Beta Brass
Phys. Rev. B12, 2125-2131 (1975)

R. B. Schwarz and A. V. Granato
Measurement of the Force-Distance Profile for the Interaction Between a
Dislocation and a Point Defect
Phys. Rev. Lett. 34, 1174-1177 (1975)

W. F. Weston and A. V. Granato
Cubic and Hexagonal Single-Crystal Elastic Constants of a Cobalt-Nickel Alloy
Phys. Rev. B12, 5355-5362 (1975)

A. V. Granato
Dislocation - Defect Interactions and Mechanical Properties of Crystals
Proceedings of International Conference on Radiation Damage in Solids, Gatlinburg,
1975 (to be published)
Also supported by NSF

M.S. Theses: (Calendar Year 1975)

None

Ph.D. Theses: (Calendar Year 1975)

David Thomas Read (A. V. Granato, Adviser)
Bias Stress Detection of Dislocation Resonance in Lead
May 1975

Defect Properties of Solids

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

Supporting Agency: U. S. Energy Research and Development Administration

Senior Staff: David Lazarus, Professor
John P. Bense, Research Associate (Term 12/31/75)

Junior Staff: Paul C. Allen, Research Assistant
Genghun Eng, Research Assistant
Mark S. Jackson, Research Assistant
Arthur E. Pontau, Research Assistant

Object: The chief aim of this project is to develop quantitative, atomistic models for describing defect and electronic properties of classic, prototypic solids, in the hope that this will lead to the eventual development of new and useful materials. In a wide variety of applications, solid materials are limited in their utility by plastic deformation, fracture, corrosion, radiation embrittlement, wear, fatigue, and a host of other ailments; improvements to existing technological materials are found through alloying, heat treatment, cold and hot working, and other forms of metallurgical art. Common to all these processes is the basic element of mass transport--diffusion within solids. The interflow of atoms accounts for the limitations of solids as well as for the cures to these limitations. Our concern is with the atomistic aspects of the basic diffusion process to isolate the electronic and structural variables which govern the rates at which both host and impurity atoms can migrate. Prior work by our group and others has demonstrated that the basic process is clearly governed by the existence of lattice defects--vacancies, interstitials, and possibly more complex mechanisms--and that a full knowledge of the diffusion process can only come from a detailed understanding of the underlying lattice defects.

Considerable work has been devoted previously to studies of diffusion in fcc metals and alkali halides, both close-packed structures, and a vacancy-type mechanism has been unambiguously identified for these cases. Current work centers around two different basic lattices: the "anomalous" bcc transition metals, typified by Ti, and the "superionic" conductors, typified by AgI and RbAg_4I_5 . Both these classes of materials show extraordinarily large diffusion coefficients, departures from Arrhenius behavior in their temperature dependences, and large differences in qualitative behavior from the "rules of thumb" for scaling diffusional phenomena and melting behavior in "normal" materials such as fcc and hcp-structured solids and most bcc structures. Our current work centers on trying to ascertain whether a basic vacancy mechanism is operable in these "anomalous" cases, or whether new defect models must be invoked.

Measurements are made using precision radiotracer techniques, supplemented, for insulators, by ionic conductivity measurements. Studies of diffusion as a function of temperature permit determination of the basic enthalpy changes associated with the fundamental process; studies as a function of strictly hydrostatic pressure (in a gas high pressure system to ensure that additional defects are not introduced by plastic deformation in the pressurization process) yield values of the elementary volume changes associated with formation and motion of defects. Studies of the mass dependence of diffusion (isotope effect) permit deduction of correlation effects fundamental to the basic measurement. It is only by a combination of these techniques that precise information about the defects responsible for diffusion can be elucidated.

Since impurity and host atoms usually diffuse at different rates in solids, we are also concerned with learning about the electronic structure of defects and of impurity atoms, and their interactions with the lattice electronic structure. Currently measurements are being made to search for possible anomalies in the electrical noise in TaS_2 and TaSe_2 , in which charge-density waves have been identified by neutron diffraction, to see whether or not these perturbations give rise to large many-body fluctuations in the density of charge carriers which would limit the validity of single charge carrier models. These studies will also be extended to the superionic conductors, where, possibly, very large charge carrier densities are involved.

Most of the experimental and theoretical work has centered about studies of diffusion in equilibrium systems, but some effort has also been directed toward non-equilibrium cases of diffusion under electrical (electromigration) and thermal gradients (thermomigration).

Results, FY 76:

Most Significant Accomplishments: Preliminary data have been obtained through high pressure studies of ionic conductivity in RbAg_4I_5 , which show that the charge transport process in the superionic regime is characterized by a very small, negative activation volume, implying that the basic charge transport mechanism is, most probably, by interstitials in this phase. A pressure effect has also been noted on the second-order phase transition in this phase; the temperature of this transition apparently changes with pressure in a highly nonlinear manner. The implications of this phenomenon are not yet understood.

Other Results: Work is nearing completion on studies of the isotope effect of two tin tracers co-diffusing in Ti. This program has encountered major technical difficulties in the past year due to the necessity for developing some new, precision radiochemical techniques for separating the tracers from the matrix, but should be completed by the end of the year.

Work is progressing on studies of diffusion of aliovalent impurities in alkali halides to test out a new theoretical model for the effect of the tracer impurities on the local vacancy concentration, extending studies completed earlier with divalent impurities.

The noise studies in dichalcogenides have produced no useful results to date because of major problems encountered in developing noise-free electrical contacts for these materials to study "flicker"-type $1/f$ noise in the presence of dc currents. No excess "white" noise of the usual Johnson variety is found anywhere in the temperature range of interest, at either the upper or lower phase transitions; in the absence of dc currents, the noise is that of a pure resistor of the same value, even very near the phase transitions.

Results Expected, FY 77: All the current programs should be completed or, if they prove intractable, abandoned. New programs will be started to extend the conductivity measurements in the superionic silver iodides, including tracer measurements, if suitable low-temperature techniques can be developed. (E.g., in RbAg_4I_5 , diffusion of Ag is so rapid at room temperature that an evaporated layer of silver can be seen visually to disappear into the matrix within hours at room temperature! Clearly conventional tracer deposition-diffusion-sectioning techniques are totally unsuitable for studying these materials.) Other superionic materials will also be investigated, and studies will be undertaken to see if there is excess noise associated with the phase transitions (again, if low-noise electrical contacts can be developed). A new program of investigation of the effect of pressure on the behavior of micromagnetic alloys is planned, in collaboration with Professor P. A. Beck.

Results Expected, FY 78: Programs initiated in FY 77 should be nearing completion, and, hopefully, will suggest new directions. The current program may branch out into totally new directions: e.g. to studies of wear (tribology) phenomena, which have received remarkably little attention from a basic research viewpoint, which are clearly of enormous technological importance, and where the a priori parallels to diffusional phenomena (never studied in detail) are, at the least, intriguing.

Relationship to Other Federally Funded Projects: None of our work directly duplicates research done elsewhere. Through meetings, exchange of preprints, and correspondence, we maintain close contact with other groups around the world working in related areas. Particularly close contact is maintained with the groups at Argonne National Laboratory, the University of North Carolina, and the Centre d'Etudes Nucleaires at Saclay, France, where a large fraction of the best work on diffusion is maintained. Within MRL, our work in superionic conductors is carried out in close collaboration with the programs of Professors Flygare, Klein, McMillan, and Salamon who are studying other aspects of these materials. Similarly, our studies of the dichalcogenides complements those of Professors Brown and Salamon. We have also worked collaboratively with Professor Holonyak in studies of the effects of high pressure on charge transport and luminescence in semiconductors, and with Professor Frauenfelder of the Physics Department on studies of the effect of pressure on the kinetics of hemoglobin. A new collaborative effort is planned together with Professor Beck of the Metallurgy Department to study the effects of pressure on the behavior of micromagnetic alloys.

Publications: (Calendar Year 1975)

V. M. Cheng, P. C. Allen, and D. Lazarus
 Pressure Coefficient of Thermoelectric Power of Platinum/Platinum-10% Rhodium
 and Chromel/alumel Thermocouples
 Appl. Phys. Lett. 26, 6-7 (1975)

H. M. Gilder and D. Lazarus
 Role of Vacancy Anharmonicity on Non-Arrhenius Diffusional Behavior
 Phys. Rev. B11, 4916-4926 (1975)

Joan L. Mitchell and David Lazarus
 Effect of Heterovalent Impurities Codiffusing with Monovalent Tracers in
 Ionic Crystals
 Phys. Rev. B12, 734-752 (1975)

R. J. Nelson, N. Holonyak, Jr., W. R. Hitchens, D. Lazarus, and M. Altarelli
 Pressure Experiment Determination of the Direct-Indirect Transition in the
 Quaternary $\text{In}_{1-x}\text{Ga}_x\text{P}_{1-z}\text{As}_z$
 Solid State Commun. (submitted to)
 Also supported by ARPA (AFOSR), NSF and ARO(D)

M.S. Theses: (Calendar Year 1975)

None

Ph.D. Theses: (Calendar Year 1975)

None

Properties of Noble Gas Crystals

Principal Investigator: Ralph O. Simmons, Ph.D.
 Professor of Physics;
 Head, Department of Physics

Supporting Agency: U. S. Energy Research and Development Administration

Senior Staff: Ralph O. Simmons, Professor
 Donald R. Baer, Research Associate

Junior Staff: Benedick A. Fraass, Research Assistant
 Steve M. Heald, Research Assistant
 Albert T. Macrander, Research Assistant

Object: There are four different goals of this research program: 1) to determine the structure of thermal defects in quantum crystals and to elucidate the mechanisms by which atomic diffusion takes place, in a regime dominated by quantum effects, 2) to discover and to characterize the nature of solid-solid phase transitions in simple molecular crystals having orientational order as a major contribution to crystal properties, 3) to understand phonon-phonon interactions in insulating crystals having large lattice anharmonicities, and 4) to investigate the origins of apparent anomalies in the low-temperature thermal properties of low-density quantum solids, particularly bcc ^3He .

In all four cases, crystals of condensed gases are chosen as the solid materials for study, because the physical phenomena arise, in such materials, in extreme form, better separated from other effects. The phenomena can be studied in such materials over an especially large range of physical conditions: factors of more than a hundred in temperature and changes up to forty percent in solid density. Another significant advantage of these materials, as model systems for the study of solid state phenomena, is the relative ease of controlling their purity and precisely analyzing their impurity content. Finally, isotopic substitution can be used to separate physical and chemical effects and to probe alternative atomic mechanisms.

To pursue these goals, using these materials, provides formidable technical challenges and often requires the invention of new types of apparatus, and adaptations of these techniques have given other scientists the means to carry out research in other areas of materials science.

Achieving the first goals, the determination of thermal defects in quantum crystals, requires a direct method for measuring defect content. For vacancy-type defects in usual solids, differential comparisons of macroscopic length and x-ray lattice parameter changes have been demonstrated effective by the principal investigator in metals and in metallic

alloys. The current work extends and simplifies this method by confining the specimens at essentially constant volume, so that x-ray lattice parameter changes alone are sufficient. This simplification increases the sensitivity of the method and reduces ambiguities in interpretation. This is important because current theories of these thermal defects suggest that they are not localized point defects, but rather, are nonlocalized: in an extreme view, are "vacancy waves."

The literature of atomic diffusion 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 systems. In others, complexity due to the appearance of competing classical processes obscures detailed understanding. As the unraveling and application of classical explanations has proceeded, interest in quantum manifestations in atomic mobility in solids has grown. Light impurities which sit off-center in crystalline sites, and tunnel between equivalent positions or orientations, have been one kind of system studied. There are technologically important examples, such as the hydrogen in niobium systems investigated locally by A. C. Anderson, H. Birnbaum, C. P. Flynn, and M. V. Klein. But model systems chosen for scientific, not technological reasons, are also necessary, in order to explore more readily the full range of real possibilities which may need to be invoked in understanding, and possibly controlling, atomic mobility in materials.

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

The second goal, characterization of some solid-solid phase transitions due to molecular rotational ordering, is intended to form a testing ground for modern theories of phase transitions in a situation of controlled complexity. By "controlled complexity" is meant: the number of variable features is limited, but the relative sizes of different possible contributions are comparable so that the resulting phenomena depend very sensitively upon the magnitudes of these contributions.

Solid methanes are attractive model systems for these purposes. Counting isotopic substituted (deuterated) cases, there are five different methanes. They show certain systematic features in the phase transitions of the pure methanes and of their mixtures. All the molecules are simple electron closed-shell configuration. The crystal phases are mostly cubic. Yet total nuclear spin and molecular rotational moments of inertia can be varied over a broad range. And a wide variety of experimental techniques (x-ray, neutron, NMR, optical, calorimetric, dielectric, and spectroscopic) can be applied.

The third goal, understanding anharmonicity in insulators, is a traditional one, first raised clearly by Max Born almost forty years ago. But advances in microscopic understanding are confined to the last decade. Our own contributions in this area have been made by showing that precise measurements on noble gas solids are possible and, from the results of such measurements, severe constraints are put upon the acceptability of theoretical formulations of the problem. These close constraints have proven useful in a situation where good knowledge of the interatomic interactions can be applied to discern an inadequate formulation of the theoretical treatment, contrary to the usual situation where they are intertwined.

The practical importance of lattice anharmonicity in electrical insulators arises, of course, from the fact that it provides a mechanism for the transport of heat and it gives rise to thermal expansion, to temperature dependence of the elastic properties, etc. Applications of solid materials in technology, not only for mechanical construction but also for component elements in solid-state electrical devices, often depend upon the thermal properties of these materials.

Our studies of thermal expansion and of elastic properties have been complemented by Raman scattering measurements in pure noble gas solids and in their mixtures. The latter yield essentially direct information about the lowest order anharmonic lattice properties.

The fourth goal, investigation of anomalies in the extreme low-temperature thermal properties of solid ^3He at low densities, arises because similar apparent anomalies may appear in disordered insulators such as glasses. As knowledge about regular crystalline materials has accumulated, scientific interest has increasingly shifted to disordered systems. At the same time, the importance to technology of certain disordered or quasi-amorphous insulators (including optically transparent ones) and semiconductors has risen.

Whether the sources of these apparent anomalies in solid helium are static or dynamic, intrinsic or extrinsic, is unknown. Existing calorimetric and elastic data are not compatible, except through ad hoc relations. We want to use well-characterized crystalline specimens to see whether the apparent anomalies persist under such conditions. We believe that x-ray diffraction and scattering techniques are the best way to proceed.

Results, FY 76:

Most Significant Accomplishments: The activation energies for formation of thermal vacancies have been measured for bcc ^3He over the range of molar volumes 19 to 24.5 cm³/mole. They are essentially identical to diffusion energies determined by NMR methods over the range 19 to 23 cm³/mole, which demonstrates that thermal vacancy motion occurs by a tunneling mechanism. The defect energies are lower than those previously inferred indirectly from heat capacity measurements at large molar volumes. A train of argument, based upon the directly measured vacancy content, leads to

an estimate of the "band width" of the "vacancy waves." The molar volume dependence of the vacancy formation energy can be analyzed to obtain the first direct measurement of the volume of formation of these (somewhat nonlocalized) thermal defects.

Other Results: Preliminary measurements of thermal vacancy energies in hcp ^3He (again compared to NMR work) show that, unlike non-close-packed bcc ^3He , vacancy migration involves thermally-activated hopping over a barrier.

Our precise lattice parameter measurements and thermal drift studies in solid CH_4 and CD_4 have produced many results.

- a) The upper phase transitions in both CH_4 and CD_4 are first-order, contrary to most previous experiments, and the characteristic time constants in pure material are extremely long (days to weeks).
- b) The latent heats of these upper transitions can now be determined with some consistency.
- c) In CD_4 the lower phase transition is to a tetragonal phase, its parameters have been accurately determined down to 4 K, and its habit of formation from the adjacent cubic phase observed.
- d) In CH_4 no lower structural phase transition appears at low temperature, but the crystal shows negative thermal expansion, which can be explained by the conversion of spin isomers on the disordered sublattice.
- e) Thermal drift measurements have established the identity (contrary to reports in the literature) of the structural and calorimetric transition temperatures.
- f) The equilibrium thermal expansion coefficients have been determined in both CH_4 and CD_4 , and R. J. Meyer (of W. L. McMillan's group) has devised a Landau theory of the upper transition (the order parameter of his theory is a third-rank tensor!).

The experimental part of our Raman scattering work, in cooperation with M. V. Klein, has been completed on argon and argon-krypton mixtures at a range of pressures up to several kilobars. The measurements extend up to 50% greater frequency shifts (i.e. to much weaker scattering) than previous work in other laboratories. Preliminary interpretations of the "one-phonon" and "two-phonon" spectra have been made and were reported verbally at APS meetings; manuscripts are in preparation. The "two-phonon" spectra are fairly direct evidence about anharmonicity which can be used to check current "self-consistent phonon" theories.

Results Expected, FY 77: Successful thermal vacancy studies on pure bcc ^3He invite serious attempts to discover modifications of these effects in ^3He - ^4He mixtures, which have been the subjects of many NMR studies. The non-localized nature of the thermal defects should be influenced not only by the masses of the atoms but also by their differing statistics. These effects, if observable, may be a way to sort out the microscopic nature of the defects; as non-localized defects ("wave packets"?), the basis states, as it were, may form a very novel set.

The verification of tunneling as the migration mechanism for the thermal defects, and the determination of the defect volume of formation in bcc ^3He , leads to confidence that the hcp ^3He phase merits more investigation, because it is clearly qualitatively different (yet the same chemically). X-ray measurements of thermal defect content in hcp ^3He and hcp ^4He will be made. With luck, some idea of the processes of vacancy generation/annihilation at dislocation sources/sinks can be obtained by comparing the relative changes in axial and orthogonal lattice parameters in the hcp phase.

An inventory of phase transitions in other crystals, besides the methanes, composed of tetrahedral molecules has already been made. The value of precise x-ray lattice parameter work on several of these more complex crystals, versus the value of Debye-Waller x-ray, elastic wave velocity, compressibility, and/or thermal drift measurements on the methanes will be decided. It will be necessary to pursue some theoretical analyses for a significant time during this time period before it is known whether the many experimental results obtained during FY 1976 are decisive for the understanding of the structural orientational ordering.

Our dilution refrigerator cryostat will be used to carry out x-ray scattering and diffraction studies in bcc ^3He in the range 0.04 to 0.6 K, in pursuit of structural characterization of the apparent thermal anomalies observed previously by others.

The question of charged defects in these insulators will be explored. Phase equilibration phenomena will be explored, both in the methanes near solid-solid transitions and in the heliums near the melting line. Relations to phenomena in amorphous materials will be sought.

One activity, for which our group has been approached in the past, but which we have not had much capacity to respond to, is "service" or cooperative projects dependent upon our high-precision x-ray cameras, diffractometers, and versatile cryostats. It is likely that during FY 1977 we can begin to respond to such requests from other MRL personnel in selected cases. Our apparatus can be applied, of course, to essentially any crystalline materials.

Results Expected, FY 78: The natures of the thermal defects in solid helium and in solid helium mixtures appear so unusual that the results of continued study are quite unpredictable. It does appear likely that the useful x-ray studies of these phenomena will not be completed during FY 1977.

Should "glassy" properties be discovered in our crystalline ^3He at extreme low temperatures, attempts at elucidation of that would extend into FY 1978.

High temperature materials remain a planning target for us. We hope to apply our expertise obtained in phase transition studies on the methane systems.

Relationship to Other Federally Funded Projects: Studies of self-diffusion, atomic, or ionic transport in quantum crystals are presently carried out at the University of Massachusetts, Case-Western Reserve, Bell Laboratories, the University of Sussex (United Kingdom), CEA Saclay (France), Institute of Physical Problems (Moscow), the Physico-Technical Institute (Kharkov), and occasionally elsewhere. The speculative content of current theoretical formulations is presently large. There is a richness among this speculation, however, which encourages hope that some truly new phenomena will be identified and established.

Studies on phase transitions in solid methanes are presently carried out at Harvard University, the University of California, Berkeley, McMaster University (Canada), the University of Toronto, KFA Julich (Germany), Grenoble (France), and several Japanese laboratories.

Raman scattering studies on noble gases and their mixtures have been carried out at Bell Laboratories. Brillouin scattering work has been done at the Universities of Toronto (Canada) and Munich (Germany). Theoretical and computational work of greatest recent significance has been produced at IBM San Jose and at NRC Ottawa (Canada). Phonon dispersion has been measured at Brookhaven National Laboratory.

The thermal anomalies in bcc ^3He were discovered at the Ames Laboratory and confirmed later at the University of Florida. Speculation about the possible origins of these anomalies has come from physicists all over the world.

In all the above cases, theoretical and experimental work on the systems cited, in the U. S. national laboratories and in U. S. universities (and indeed the other labs, too), complements the present project but does not duplicate any portion of it.

Publications: (Calendar Year 1975)

V. M. Cheng, W. B. Daniels, and R. K. Crawford
Melting Parameters of Methane and Nitrogen from 0-10 Kilobars
Phys. Rev. B11, 3972-3975 (1975)
Also supported by NSF GP-7739 and GP-18573 (U. of Delaware)

R. K. Crawford, W. B. Daniels, and V. M. Cheng
Melting and Its Relation to Molecular Orientations in the Fluid and Solid Phases of N_2 and CH_4
Phys. Rev. A12, 1690-1696 (1975)
Also supported by NSF GH-32491X and Unidel Foundation (Delaware University)

R. K. Crawford, W. F. Lewis, and W. B. Daniels
Thermodynamics of Solid Argon at High Temperatures
Solid State Phys. C (to be published)
Also supported by NSF GH-32491X

L. A. Schwalbe
Equilibrium Vacancy Concentration Measurements in Solid Argon
Phys. Rev. B (to be published)

M.S. Theses: (Calendar Year 1975)

None

Ph.D. Theses: (Calendar Year 1975)

D. R. Aadsen (R. O. Simmons, Adviser)
Lattice Parameter and Thermal Expansion in Solid Methane
October 1975

Nuclear Magnetic Resonance in Solids

Principal Investigator: Charles P. Slichter, Ph.D.
Professor of Physics

Supporting Agency: U. S. Energy Research and Development Administration

Senior Staff: Charles P. Slichter, Professor
Stephen F. Meyer, Research Associate

Junior Staff: Daniel Abbas, Research Assistant
Thomas J. Aton, Research Assistant
Stephen H. Couturie, Research Assistant
James P. Long, Research Assistant
Howard E. Rhodes, Research Assistant

Object: (A) Magnetic Atoms in Non-Magnetic Metals. We are studying two broad aspects, which, however are closely related: (1) the Kondo effect, a challenging many-body problem; and (2) the general nature of electronic structure of the magnetic atoms.

The Kondo effect is an important theoretical problem both because the theoretical problem is similar to ones encountered in other parts of physics, such as the explanation of the effect of electron-electron interactions on the optical and x-ray properties of solids, and because it has led to discovery by Wilson, Krishna-murthy, and Wilkins at Cornell of important new theoretical methods for dealing with solids.

Our experiments consist of studying the nuclear resonance of Cu^{63} nuclei which are near neighbors of iron group atoms present in dilute alloys (.01% to 1% atomic fraction of iron group atoms in copper). The magnetism of the iron group atom induces a cloud of magnetization in the conduction electrons in the vicinity of the iron group atom. Our measurements enable us to produce a map of that induced magnetization at, in some cases, five or six nearby shells of Cu nuclei. From such measurements it is possible to deduce the energies and widths of the energy levels of the iron group atoms, information which has not heretofore been measured. These results are basic to understanding the magnetic properties of the iron group atoms: why Cr, Mn, and Fe are strongly magnetic in Cu, whereas Sc, Ti, V, Co, and Ni are not.

Recently, Wilson, Krishna-murthy, and Wilkins have shown how to predict the observed Kondo effect starting from a simplified picture of the magnetic atom, making assumptions only as to the energy and width of the energy levels of the magnetic atom, just the quantities our experiments are able to provide. Their model is simplified in the sense that it assumes the magnetism arises from s-electrons, whereas in fact it arises from d-electrons. If the theory can be extended to treat d-electrons, the theory will provide a complete first principles prediction of the Kondo effect to test against measurements. The

measurements we are carrying out will provide knowledge of the input data about the magnetic atom which, when used, leads to a definite prediction of the Kondo temperature. Comparison of the predicted and measured Kondo temperatures would thus provide a complete test of such a first principles theory. We are fortunate in having recently received acceptance by Dr. Krishna-murthy of a postdoctoral position at Illinois.

We believe such a test would make a significant contribution to understanding basic properties of solids. It will also provide an understanding of the Kondo effect at a vastly deeper level than had previously been thought possible.

(B) Transition Metal Dichalcogenides 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 metal 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 tuneable by selection of the molecular species intercalated as well as the ratio of intercalate to host 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 feel these compounds are important to study both because of the light they may shed on the practical problem of how to raise T_c of a superconductor, but also because, as the first materials known to exhibit charge density waves, they have opened a new field of important new science related to electrical conduction. They are closely related to the phenomenon of spin density waves (exhibited by Cr) which is an important cause of magnetism. Thus, we judge that these compounds provide an excellent chance to explore new realms of electrical conduction, superconductivity, and magnetism, all important fields technically for production and transmission of energy.

We are studying aspects of intercalation and of charge density waves.

In the area of intercalation, Dr. Meyer of the resonance group is studying TaS_2 containing H, a system he studied for his Ph.D. thesis at Stanford. He found that intercalation by H causes the superconducting transition temperature, T_c , to go through a maximum (with T_c nearly three times as high as for pure TaS_2) as the H concentration is increased. He postulated that as the H atoms go into the TaS_2 , they give up their outer electrons to the conduction band. As more hydrogen goes in, the Fermi energy rises through the conduction band. According to the BCS theory, T_c depends on the density of states at the Fermi energy, $N(E_F)$. Meyer suggested that it is the variation of $N(E_F)$ as the H electrons fill the conduction band which is responsible for the change in T_c .

We are measuring the proton spin-lattice relaxation rate since the contribution of the conduction electrons to that quantity is proportional to $N(E_F)$ giving us a means of testing the proposed explanation for the variation in T_c on intercalating hydrogen.

We are studying charge density waves. The wavelength of a charge density wave is found at the lowest temperatures to be commensurate with the lattice (e.g. three times the lattice constant) but at somewhat high temperatures it is incommensurate. The earliest view of the incommensurate wave was that it was a pure sinusoidal modulation whose phase, therefore, slipped in a regular manner with respect to the lattice as one moved along the charge density wave. Professor McMillan of our department has proposed an alternative picture, that the incommensurate phase consists of a charge density wave which is commensurate except over a small region over which there is a phase slip. He calls these regions of phase slip "discommensurations." Such a picture is similar to the way a dislocation accounts for slip. It should be possible to distinguish the two proposed pictures by NMR. For a commensurate CDW in TaS_2 , there should be a set of discrete Ta^{191} NMR lines, one for each distinct position of a Ta nucleus on the wave. If McMillan's picture of discommensurations is correct, these NMR lines should persist when one passes into the incommensurate phase, since most Ta nuclei will be in a commensurate region. But if the CDW is uniformly incommensurate, the NMR lines will consist of a smooth smear. Thus, the spectra differ in the two cases.

(C) Catalysis. The successes we have had in our studies of dilute systems of magnetic atoms in non-magnetic metals have stimulated our interest in other areas of major scientific and practical importance requiring high sensitivity in detecting nuclear resonance. We are currently investigating potential problems in catalysis, an area which is vital to many areas of physics, chemistry, and biology and of particular importance to production and usage of fuels.

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

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

Although typically the platinum atoms are less than 1% of the atom numbers in the catalyst, we believe the fraction of atoms on the surface is sufficiently large that there is a good chance of seeing their resonance using the sensitive methods we have previously employed.

Platinum, being a spin 1/2 nucleus, is not troubled by quadrupole interactions, but its very large Knight shift of several % should be different for surface atoms from those on the interior. Moreover, depending upon what crystal face forms a surface, the Knight shift might differ.

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

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

We have observed the Pt resonance in 1000 Å particles. We have had an interesting and fruitful interaction with Dr. John Sinfeld of Exxon, well known for his pioneering studies of catalysts. We have met with him and discussed our concepts of what one might learn from nuclear resonance studies. Following these discussions, he kindly prepared a set of samples for us consisting of Pt particles on alumina, the different samples differing in Pt radius. The radii go from 10 Å in a sample to 40 Å in another. We are currently working on these samples.

(D) A New Method for Electrical Conductivity Measurements. The conventional method of measuring electrical conductivity is the four probe method. In the last several years, the subject of conductivity measurements has interested many people because of the surprisingly high values reported by Heeger and his colleagues for the highly anisotropic organic electrical conductor TTF-TCNQ at temperatures near 80 K. He suggested there might be a relationship of his results to superconductivity. Other workers proposed that his results were artifacts of poor or misaligned contacts in his four probe experiments. Stimulated by the potential importance of understanding the conductivity of compounds such as TTF-TCNQ, we have devised a new method for measuring conductivity, one which will enable us to use a moving contact and thus to provide a self-check which we hope will assure that the results are valid.

The method involves putting the sample in a scanning electron microscope. Two contacts are attached to the sample. One is connected to ground. A voltmeter (actually a lock-in amplifier driving a chart recorder) is connected between the other and ground. Current is injected into the sample by the beam of the microscope. Modulation of the beam position along the sample modulates the voltage measured by the voltmeter. The change in voltage for a given modulation amplitude and for a known current gives one the conductivity. Since one can move the beam continuously around on the crystal, one can check that the current flow patterns are well behaved, or whether, perhaps because of micro-cracks or poor contacts, they are not.

Results, FY 76:

Most Significant Accomplishments: (1) We have shown that our measurements in powders and single crystals of dilute alloys CuFe enable us to determine the electronic structure of the Fe atom in Cu. This has never been done before for the Fe group atoms in non-magnetic hosts. Specifically, we have deduced the position of the energy levels, the width of the energy levels, have shown that there is a crystal splitting of the iron d-levels and have measured it, and that the Fe atom has 7.0 d-electrons. We have thus evaluated for the first time the quantities involved in P. W. Anderson's theory of magnetic atoms in non-magnetic metals.

These results have added significance as a result of the success of Wilson, Krishna-murthy, and Wilkins in showing how, given information such as we have obtained, one can predict a Kondo effect and calculate a Kondo temperature to compare with experiment. As yet their theory does not apply to d-electrons as is necessary to discuss the experiment, but if it is possible to extend their theory to d-electrons one will have achieved a first principles understanding of the Kondo effect with all quantities which go into the theory or are predicted by the theory known from experiment. Such a theory, using our experimental results, would achieve a depth of understanding of the Kondo effect which no one dreamed would be possible several years ago, truly a major advance in understanding magnetism.

(2) We have succeeded in carrying out single crystal studies of the dilute alloys CuCr, and CuMn. As a result, we have high hopes of deducing the same information for these alloys that we have for CuFe—namely, the details of the electronic structure.

(3) Our results for CuCo single crystals prove unequivocally that one must include a crystal splitting of the Co energy levels to understand the magnetic properties of Co in Cu. As mentioned above we find that we also need a crystal splitting to explain the CuFe data and deduce the size of the splitting. We hope to deduce the size for Co as well.

These results are the first proof of the importance of crystal splittings in understanding the magnetic properties of iron group atoms in metals.

(4) We have studied the system CuCr from room temperature to liquid neon temperature (about 27 K). Our studies demonstrate that either the susceptibility deviates significantly from the usual Curie-Weiss law obeyed by other magnetic atoms in non-magnetic hosts, or else the previously deduced Kondo temperature of this system is in error.

Other Results: (A) Iron Group Atoms in Cu. In addition to the results described above, we have completed studies of the systems CuSc and CuTi. We find that they are very weakly magnetic, comparable to CuNi. We have proved the correctness of our conjecture that the CuSc samples contain Cu resonance from the compound CuSc as well as from Cu near to isolated Sc atoms. Thus, our NMR data give metallurgical data for the CuSc system as to solubilities just as they did for CuV.

(B) Transition Layer Dichalcogenides.

(1) Intercalation. We have prepared a series of samples of TaS_2 containing different concentrations of H. We have begun measuring the proton spin-lattice relaxation time, T_1 , and the relaxation time $T_{1\rho}$ for these samples over a temperature range from 1.3 K to 300 K. We observe a conduction electron contribution for the samples we have completed. We do not as yet fully understand the data, but expect to be able to as we complete the data collection.

(2) Charge Density Waves. We have grown single crystals of TaSe_2 and TaS_2 to look for the Ta and Se resonances. In the TaSe_2 , we have observed the Se resonance using a magnetic field of 10,000 gauss, at 4.2 K and 300 K. Selenium has a nuclear spin of $1/2$. It could in principle reveal a charge density wave through the effect of the CDW on the Knight shift. Each distinct Se location in the CDW should have a characteristic Knight shift, giving rise to structure on the Se NMR. At 10 k gauss we do not detect any such structure. We will use our superconducting solenoid to go to 60 k gauss to enhance any splittings which might exist.

(C) Catalysis. We have prepared samples of 1000 Å Pt particles in light oil, and have observed the Pt nuclear resonance in them. We are investigating means of optimizing the signal to noise. We have had discussions with Dr. John Sinfeld of Exxon, an expert in catalysis, who has provided us with several well-characterized samples for study. We are currently investigating them.

(D) Electrical Conductivity of TTF-TCNQ. We have designed and constructed a cold stage to enable us to study the conductivity of TTF-TCNQ single crystals in the scanning electron microscope as a function of temperature. We have carried out studies to determine the optimum beam current and beam voltage for these studies to take account of possible radiation damage to the sample, and secondary electron emission. We have also perfected an electronic beam alignment method to enable us to make fine adjustments of the direction of beam modulation with respect to the physical orientation of the crystal.

Results Expected, FY 77: (A) Dilute Alloys of Iron Group Atoms in Cu. We hope to determine the energy level structure of Mn and Cr atoms in Cu by analysis of our single crystal data. These data will serve as input to a theoretical prediction of the Kondo temperature for these systems if the theorists can extend the results of Krishna-murthy, Wilson, and Wilkins to d-electrons.

As part of the results on the electronic structure, we hope to deduce the crystal splittings of the d-states, and the number of d-electrons these atoms possess when in Cu. These results have never been known before.

At present the Kondo temperature of the system CuCr has been deduced only somewhat indirectly through spin transmission measurements. Our experiments on CuCr have shown that either the value deduced is incorrect, or else there are substantial deviations from the usual Curie-Weiss behavior. We will try to settle this question by carrying our satellite studies to liquid helium temperatures.

(B) Transition Metal Dichalcogenides.

(1) Intercalation of Hydrogen. We expect to complete our studies of the NMR of protons, to see whether or not the data support the prior conjectures as to why intercalation with hydrogen changes the superconducting transition temperature.

(2) Charge Density Waves. We will study the Se resonance at 60 k gauss in single crystals of TaSe_2 at 4.2 K to see whether or not there is resolved structure indicative of the existence of the charge density wave. If there is, we will go to temperatures in which the charge density wave is incommensurate with the lattice to test McMillan's theory of how the incommensurate wave fits into the lattice.

We will continue our search, so far unsuccessful, for the Ta nuclear resonance.

(C) Catalysis. Essential to our plans is observation of the Pt resonance in very small particles such as those provided us by Dr. Sinfeld. We will try to observe the Pt resonance in these samples. If successful we will search for surface resonances.

If not successful, we will prepare samples of larger radius to find what happens to the resonance as the radius decreases, and thus to see what we must do to find the resonance in very small particles.

(D) Conductivity of TTF-TCNQ. We expect to complete conductivity experiments on a group of single crystals to determine the frequency and characteristics of crystal imperfections which distort the current flow pattern from the ideal, and to use data on crystals whose flow pattern we know to be ideal to measure conductivity versus temperature.

Results Expected, FY 78: (A) Magnetic Atoms in Non-Magnetic Metals.

There is a substantial chance that we will wish to do further data analysis of data we are currently taking, and theoretical work to explain the data. For example, we have data on pseudodipolar and electric quadrupole couplings which should provide independent evidence on the electronic structure of the magnetic atoms. We have concepts which we think will account for these data, but they involve computing out numerical integrals.

Thus we hope to understand why the pseudodipolar and electric quadrupole couplings have the values they have, and to use those values to confirm the electronic structure of the atoms.

(B) Transition Metal Layer Compounds. Some important scientific questions about the transition metal layer compounds are (1) what is the amplitude of charge density waves, and what determines the amplitude, (2) how do incommensurate charge density waves fit into the lattice, (3) what are the dynamical characteristics of charge density waves, and (4) is the existence of charge density waves and their corresponding lattice distortions related to the existence of superconductivity as has been suggested might be true for the A-15 compounds.

These several questions indicate the importance of being able to deduce the amplitude and detailed form of charge density waves, exactly the sort of information we are studying by nuclear magnetic resonance.

Two key aspects for such work are the use of single crystals (which we are doing) and observation of the appropriate nuclear resonance. We are placing heavy emphasis on finding the Ta¹⁹¹ nuclear resonance, because we expect it to have large electric quadrupole coupling, which would make it especially suitable for studying charge density waves. Our heaviest emphasis will be on finding and using the Ta¹⁹¹ resonance to study the charge density waves.

(C) Catalysis. We plan to continue work on catalysis using large surface area (small particle) catalysts. Since we are still in the opening stages, we do not yet know what the opportunities will be. But we believe magnetic resonance has great potential for studying the structure of catalysts themselves, or deducing the chemical species which exist during catalytic steps. We will push this work as fast as technical progress permits.

(D) One Dimensional Conductors. At present it is not clear whether or not the conductivity of these materials can be understood as simple one-electron conductivity, or perhaps requires collective processes. What chance we have to help resolve these matters depends on the quality of results we obtain this spring. We will exploit to the full the unique features of our method (1) that it can observe whether or not the current flow is well-behaved (i.e., not subject to the lead misalignment errors which can plague the conventional methods), (2) that it can measure local conductivity, thus detect high values which might be associated with especially perfect portions of a crystal, and (3) that we inject through the surface layers by use of appropriate electron energies.

Relationship to Other Federally Funded Projects: We have an informal relationship with Professor Geballe's group at Stanford who are doing work on transition metal chalcogenides. Dr. Meyer, of our group did his Ph.D. on these compounds with Professor Geballe. We use different experimental methods, so the work is complementary.

We are in close contact with Dr. Follstaedt and Dr. Narath of Sandia who are working on magnetic atoms in non-magnetic hosts. We are also exchanging information with Drs. Krishna-murthy, Wilkins, and Wilson at Cornell on the relation of our experiments to their Kondo theory.

We are collaborating with Professor W. McMillan of our own department who is doing theoretical work on these substances, and with Professor F. Brown who is planning to study Fermi surfaces using photoemission of electrons.

Publications: (Calendar Year 1975)

Charles P. Slichter

Some Scientific Contribution of Herbert S. Gutowsky

J. Magnetic Resonance 17, 274-280 (1975)

James B. Boyce and Charles P. Slichter

Conduction-Electron Spin Density Around Fe Impurities in Cu Above and Below the Kondo Temperature

Phys. Rev. (submitted to)

J. B. Boyce and C. P. Slichter

Determination of the Energy Level Parameters and Crystal Field Splitting for Fe in Cu

Proceedings Conference on Magnetism and Magnetic Materials, Philadelphia, Pa., 1975 (to be published)

D. Follstaedt and C. P. Slichter

An NMR Search for Charge Density Waves

Phys. Rev. (submitted to)

C. P. Slichter

NMR Studies of the Kondo Effect Revisited

Proceedings Conference on Magnetism and Magnetic Materials, Philadelphia, Pa., 1975 (to be published)M.S. Theses: (Calendar Year 1975)

None

Ph.D. Theses: (Calendar Year 1975)

David Martin Follstaedt (C. P. Slichter, Adviser)

A Nuclear Magnetic Resonance Study of Dilute Copper-Vanadium Alloys

January 1975

ED-02-02-04-0 Particle-Solid InteractionsRadiation Damage in Solids

Principal Investigator: James S. Koehler, Ph.D.
Professor of Physics

Supporting Agency: U. S. Energy Research and Development Administration

Senior Staff: James S. Koehler, Professor
Gerhard H. H. Fritsch, Research Associate

Junior Staff: Walter S. Knodle, Research Assistant (Term 3/11/76)
Robert Kozlowski, Research Assistant
Maria A. Menendez, Research Assistant
James Watson, Research Assistant

Object: We are attempting to examine point defects and defect clusters in all metals. First, we study pure metals. We would like to determine the geometrical structure, the formation and migration energies and the physical property changes associated with the presence of defects in solids resulting from irradiation. We seek general laws. For example, the finding that the temperature of the highest close pair peak is linearly related for all fcc metals to the Debye θ is a generalization. We want an understanding of this result on an atomic level.

At present most pure fcc metals are reasonably well understood (except gold). We are therefore shifting emphasis to bcc and hexagonal metals.

Once pure metals are reasonably well understood, we plan to seek an understanding of the interactions and interrelations between point defects and impurities. For example: do gaseous impurities alter Stage III annealing of copper and silver? We are doing an irradiation experiment of pure silver at 100 K and at 10^{-9} Torr to answer this question. We need to measure impurity interstitial trapping energies for various impurities in both fcc and bcc metals. At present we know that atomic core size effects are important for fcc metals. We guess they are not as important for bcc metals, but we need data.

We need geometrical information concerning point defects and defect impurity clusters which can be obtained if an energy analyzer for the electron microscope becomes available.

On the theoretical side, we are attempting to calculate the formation energies, the migration energies, and the low frequency resonant vibrations of interstitials in bcc metals. We believe that we have acceptable interatomic potentials, but further comparison with the data will be required.

We are just beginning to do theory for hexagonal crystals. At present no one knows the interstitial configuration nor do we know how an interstitial migrates in a hexagonal crystal. For hexagonal metals, we must achieve a description which distinguishes forces along the c axis from forces in the basal plane.

Results, FY 76:

Most Significant Accomplishments: We have demonstrated that there are two classes of bcc metals. One group (niobium and iron) shows high temperature Stage I annealing ($80\text{ K} \pm 20\text{ K}$). The other group shows low temperature Stage I annealing ($25\text{ K} \pm 15\text{ K}$). This probably means that the geometrical structure of the interstitial differs for the two classes. If so, the impurity interstitial trapping and the void formation will differ.

Other Results: (1) A discrete annealing step was seen in gold at 0.62 K (Birtcher, Hertz, Fritsch, and Watson, Gatlinburg Conference).

(2) The properties of divacancies in lead (i.e., the migration energy and the binding energy) have been measured by quenching and annealing.

(3) The available experiments for the fcc metals show that T_{ID} is linearly related to θ_D (i.e., the temperature associated with the Stage I_D annealing peak is linearly related to the Debye θ of the metal). (J. Koehler, Gatlinburg Conference). Gold is anomalous.

(4) For the bcc metals, there is also a linear relationship between the temperature of the highest close pair annealing process and the Debye θ . However, there are two classes of bcc metals. Each class has its own linear relation. Iron and niobium have high close pair recombination temperatures whereas tantalum, tungsten, and molybdenum give a linear relation at lower recombination temperatures. (J. Koehler, Gatlinburg Conference). A theoretical understanding of why such linear relationships exist for both fcc and bcc metals has not yet been achieved.

(5) For hexagonal metals, we have shown that the annealing at low temperatures of cadmium differs from that of zinc. In addition, some understanding of the strange annealing behavior of cadmium irradiated with thermal neutrons at 3.6 K has been achieved (J. Koehler, Gatlinburg Conference and J. Koehler, Atlanta Meeting, Am. Phys. Soc., March 29, 1976).

(6) Theory: We are making theoretical calculations concerning point defects in bcc crystals. A two-body potential is used which contains interactions between nearest and next nearest neighbors. The constants in the potential are chosen to: (a) fit the appropriate Firsov potential at small atomic separations, (b) give the correct cohesive energy and elastic constants, and (c) join smoothly together the first neighbor and the second neighbor potentials at a distance midway between the equilibrium first and second neighbor distances.

At present we are using the resulting potentials to: (1) determine which interstitial structure has lowest energy, (2) to calculate the frequencies and the geometries of the low-lying resonance modes. Thus far, calculations have been carried out for iron and tungsten. In iron the stable interstitial is the split $\langle 110 \rangle$ interstitial. In tungsten the stable interstitial is the split $\langle 111 \rangle$ interstitial.

Note that this suggests that a different linear relationship between T_{hicp} and θ_D exists for metals having different stable interstitials.

The finding that there are two different kinds of stable interstitials among the bcc metals is important because the entire annealing behavior of the two classes of bcc metals will differ. Moreover, the interaction of the two kinds of interstitials with impurities should differ.

Results Expected, FY 77: (1) We are now electron irradiating pure silver in ultra high vacuum (10^{-9} Torr) and at 100 K. We believe that gaseous impurities, particularly oxygen, result in complex annealing in Stage III in silver (i.e., in the temperature region -70°C to $+50^\circ\text{C}$). An irradiation has been made and isochronal annealing studies are underway.

(2) Gold: Pure gold is being irradiated at 0.60 K. We wish to determine whether the 0.62 K step obeys first, second, or third order annealing kinetics (i.e., is it a close interstitial vacancy pair recombination; does it involve three dimensional long-range migration of an interstitial, or is it associated with long range migration in one dimension?).

(3) Magnesium: We are electron irradiating pure magnesium at 3 K. No careful production or annealing data exists for magnesium. Magnesium is nearly close packed. We would like to determine whether the energy required to displace a magnesium atom in the c direction is the same as that required for displacement parallel to the basal plane. One irradiation has been performed.

(4) Cadmium: We have pure cadmium single crystals. We would like to determine the displacement threshold for displacements parallel to c and to a. Moreover, we would like to find out whether the annealing behavior changes when first a displaced cadmium atom does not have enough kinetic energy to penetrate a neighboring basal plane, and second, the displaced atom has more than enough kinetic energy for penetration. We have not as yet prepared single crystal specimens.

(5) Vanadium and Chromium: These are bcc metals and should be in the same class as iron and niobium. Klabunde and Coltman [Rad. Effects 7, 325 (1971)] have irradiated vanadium at 3.6 K. They saw continuous annealing except for a peak at 47 K. It is possible that their data is influenced by impurities. We have vanadium of higher purity (prepared by the Ames Laboratory).

Thus far no irradiation or annealing data exists for chromium. We hope to irradiate and anneal 99.999% pure chromium.

(6) Theory: We plan to calculate for the bcc metals the interstitial formation and migration energies. In addition, we will find the frequency and the symmetry of the low frequency resonant modes. We will begin with iron and tungsten. We hope that these calculations will confirm our separation of the bcc metals into two classes.

Results Expected, FY 78: (1) Hexagonal Metals: Of the 38 metals in the periodic table which have simple crystal structures (fcc, bcc or hexagonal), 13 are hexagonal. Their melting points range from 692.6 K for zinc to 3453 K for rhenium.

To date, very little careful irradiation and annealing data has been obtained.

First, we wish to determine whether the energy required to displace a lattice atom differs appreciably with the direction of the impulse. For magnesium which is nearly close packed and where the core size is small compared with the nearest neighbor distance, one would guess the displacement energy would not depend strongly on the impact direction (i.e., we expect E_d to vary by a factor of 2 or 3). For cadmium however, one would expect a larger variation with impact direction.

Second, for cadmium it is possible that the interstitial occupies a position in between two neighboring basal planes. If so, it can probably move thermally more easily parallel to the basal planes than perpendicular to them. This should lead to considerable trapping of one defect by another at temperatures which are low enough that thermal migration in the c direction does not occur. Cadmium and zinc with $c/a \approx 1.87$ should show such effects. It will be interesting to see whether similar effects occur for hexagonal metals which are nearly close packed.

Zirconium does not show void growth unless preinjected with helium. It does, however, have anisotropic growth under irradiation (i.e., elongation along the c axis differs from that along a).

(2) Elastic and Inelastic Electron Scattering: We would like to scatter 100 keV electrons from defects in solids. Calculations show that the geometry of point defects and of defect clusters can be obtained if the intensity of the elastic scattering between the Bragg peaks in reciprocal space is measured as a function of the scattering angles $\theta\phi$. We have an electron source, but we need an energy analyzer. This must have sufficient energy resolution to exclude the electrons which suffer plasma losses (i.e., the energy resolution should be better than 1 eV in 100 keV). Electron scattering has the advantage over X-ray and neutron scattering that more intense beams can be produced and detection and counting are easy.

We would also like to use this instrument to do inelastic scattering in which transient defects are generated in solids.

(3) Defect Relaxations: We plan to apply low frequency stresses to single crystals containing point defects. Such stresses can produce a preferred orientation of those defects whose symmetry is lower than that of the crystal. We would like to measure the resonant frequency by varying the applied frequency at constant temperature, the damping, and the amount of preferred orientation. The amount of preferred orientation can be determined by measuring length changes during a cycle.

(4) Impurities: We believe that small core impurities can trap interstitials securely in close packed metals. We would like to measure trapping energies by pulse heating to break up the impurity interstitial complex. Subsequent annealing would detect free interstitials. The initial alloys to try would be copper plus 0.1 at.% beryllium; gold plus 0.1 at.% aluminum; and platinum plus 0.1 at.% aluminum.

(5) Transient Imperfections: We believe that melting arises when thermal fluctuations generate transient local imperfections. During melting a cooperative generation of a mode of such imperfections occurs. We wish to generate such imperfections by electron scattering at temperatures below the melting temperature. Energy loss measurements of the scattered 100 keV electrons would detect generation.

Relationship to Other Federally Funded Projects: We are doing research in cooperation with Dr. Y. Lwin of Western Illinois University and with Mr. E. Ryan and Dr. J. J. Jackson of the Argonne National Laboratory. Dr. Lwin and Mr. E. Ryan are irradiating pure magnesium at 3 K. They will also study its annealing using electrical resistance measurements. Similar research on dilute lead alloys has been completed by the group.

In addition, we are obtaining pure vanadium and chromium from F. A. Schmidt of the Ames Laboratory. We plan to make electrical resistance measurements on these bcc metals.

Publications: (Calendar Year 1975)

R. Berliner and J. S. Koehler
Temperature Dependence of Transmission Proton Channeling in Ag
Phys. Rev. B12, 3559-3574 (1975)

J. Koehler
Decrease in the Void Growth Rate by Interstitial Trapping
Journal of Applied Physics 46, 2423-2428 (1975)

R. Berliner and J. S. Koehler
The Analysis of Forward Scattering Channeling Data
Radiation Effects (accepted)

R. C. Birtcher and J. S. Koehler
The Recovery of Lead After Electron Irradiation at 1.5 K
Phys. Rev. (accepted)

Masao Doyama and J. S. Koehler
The Relation Between the Formation Energy of a Vacancy and the Nearest Neighbor Interactions in Pure Metals and Liquid Metals
Acta Metallurgica (accepted)

J. S. Koehler

Interstitials in Metals

Proceedings Conference on Radiation Damage in Metals, Gatlinburg, 1975

(to be published)

M.S. Theses: (Calendar Year 1975)

None

Ph.D. Theses: (Calendar Year 1975)

Robert Charles Birtcher (J. S. Koehler, Adviser)

The Recovery of Lead After Electron Irradiation at 1.5 K

May 1975

ERDA PERSONNEL

Senior Staff

Altstetter, Carl J., Professor, Department of Metallurgy and Mining Engineering
 Amano, Muneyuki, Visiting Research Associate Professor, Department of
 Metallurgy and Mining Engineering
 Baer, Donald R., Research Associate, Department of Physics
 Beck, Paul A., Professor, Department of Metallurgy and Mining Engineering
 Benschel, John P., Research Associate, Department of Physics (Term 12/31/76)
 Birnbaum, Howard K., Professor, Department of Metallurgy and Mining Engineering
 Chen, Chee Gregory, Research Associate, Department of Metallurgy and
 Mining Engineering
 Drickamer, Harry G., Professor, Department of Chemical Engineering and
 Physical Chemistry
 Fraser, Hamish L., Assistant Professor, Department of Metallurgy and
 Mining Engineering
 Fritsch, Gerhard H. H., Research Associate, Department of Physics
 Granato, Andrew V., Professor, Department of Physics
 Hara, Kimihiko, Research Associate, Department of Chemistry
 Jennison, Dwight, Research Associate, Department of Physics
 Jonas, Jiri, Professor, Department of Chemistry
 Koehler, James S., Professor, Department of Physics
 Lazarus, David, Professor, Department of Physics
 Linowski, John W., Research Associate, Department of Chemistry (Term 1/31/76)
 Metzger, Marvin, Professor, Department of Metallurgy and Mining Engineering
 Meyer, Stephen F., Research Associate, Department of Physics
 Otsuka, Kazuhiro, Visiting Research Associate, Department of Metallurgy
 and Mining Engineering (Term 3/4/76)
 Payne, David, Assistant Professor, Department of Ceramic Engineering
 Pugh, E. Neville, Professor, Department of Metallurgy and Mining Engineering
 Rowland, Theodore J., Professor, Department of Metallurgy and Mining Engineering
 Setser, George G., Research Assistant Professor, Department of Physics
 Simmons, Ralph O., Professor, Department of Physics; Head of Department
 Slichter, Charles P., Professor, Department of Physics
 Wayman, C. Marvin, Professor, Department of Metallurgy and Mining Engineering
 Wert, Charles A., Professor, Department of Metallurgy and Mining Engineering,
 Head of Department
 Williams, Wendell S., Professor, Department of Physics and of Ceramic
 Engineering

Junior Staff

Abbas, Daniel, Research Assistant, Department of Physics
 Allen, Paul C., Research Assistant, Department of Physics
 Aton, Thomas J., Research Assistant, Department of Physics
 Au, Joseph J., Research Assistant, Department of Metallurgy and Mining Engineering
 Beggs, Dennis, Research Assistant, Department of Metallurgy and Mining Engineering
 Berker, Terrell D., Research Assistant, Department of Physics
 Bethin, James R., Research Assistant, Department of Ceramic Engineering
 Bhowal, Prabir R., Research Assistant, Department of Metallurgy and Mining Engineering
 Bieg, Kevin W., Research Assistant and GE Fellow, Department of Chemistry
 Browning, Barbara, NIH Fellow, Department of Physics
 Bruemmer, Stephen H., Research Assistant, Department of Metallurgy and Mining Engineering
 Cassidy, Michael P., Research Assistant, Department of Metallurgy and Mining Engineering
 Couturie, Stephen H., Research Assistant, Department of Physics
 Drotning, William D., Research Assistant, Department of Physics
 (Term 10/15/75)
 Eltoukhy, Atef H., Research Assistant, Department of Metallurgy and Mining Engineering
 Eng, Ganghun, Research Assistant, Department of Physics
 Fay, Roberta M., Research Assistant, Department of Ceramic Engineering
 Finston, Martin I., Research Assistant, Department of Physics
 Fraass, Benedick A., Research Assistant, Department of Physics
 Fujita, Jun Ichi, Research Assistant, Department of Metallurgy and Mining Engineering
 Fury, Michael A., Research Assistant, Department of Chemistry
 Heald, Steve M., Research Assistant, Department of Physics
 Hockert, Eric N., Research Assistant and MOCO Fellow, Department of Chemistry
 Hook, John W. III, Research Assistant, Department of Chemistry
 House, Gary L., Research Assistant and Union Carbide Fellow, Department of Chemistry
 Hughes, Scott E., Research Assistant, Department of
 (Term 9/20/75)
 Huson, Thomas E., Research Assistant, Department of Metallurgy and Mining Engineering
 Isaac, Randall D., Research Assistant and Fellow, Department of Physics
 Jackson, Mark S., Research Assistant, Department of Physics
 Johnson, David L., Research Assistant, Department of Physics
 Johnson, Roger, NIH Fellow, Department of Ceramic Engineering
 Johnson, Marvin W., Research Assistant, Department of Physics
 Kim, Myung-Hwan, Research Assistant, Department of Metallurgy and Mining Engineering (Term 9/5/75)
 Klein, David L., Research Assistant, Department of Physics
 Klick, David I., Research Assistant, Department of Physics

Knodle, Walter S., Research Assistant, Department of Physics
(Term 3/11/76)

Ko, Byung, Research Assistant, Department of Ceramic Engineering

Koch, Gerhardus H., Research Assistant, Department of Metallurgy and
Mining Engineering (Term 2/27/76)

Kozlowski, Robert, Research Assistant, Department of Physics

Labun, Lance C., Research Assistant, Department of Metallurgy and Mining
Engineering

Lenahan, Patrick, Research Assistant, Department of Metallurgy and Mining
Engineering

Long, James P., Research Assistant, Department of Physics

Macrander, Albert T., Research Assistant, Department of Physics

Matusiewicz, Gerald R., Research Assistant, Department of Metallurgy and
Mining Engineering

Menendez, Maria A., Research Assistant, Department of Physics

Mitchell, Dean J., Research Assistant, Department of Chemistry

Nelson, Joseph L., Research Assistant, Department of Metallurgy and
Mining Engineering

Park, Sang, Graduate Student, Department of Ceramic Engineering

Poker, David B., Research Assistant and Fellow, Department of Physics

Pontau, Arthur E., Research Assistant, Department of Physics

Rhodes, Howard E., Research Assistant, Department of Physics

Shalvoy, Robert S., Research Assistant, Department of Metallurgy and
Mining Engineering

Sherman, Robert, Graduate Student, Department of Metallurgy and
Mining Engineering

Shull, Robert D., Research Assistant, Department of Metallurgy and
Mining Engineering

Steckel, Gary L, Research Assistant, Department of Metallurgy and
Mining Engineering

Tortorelli, Peter F., Research Assistant, Department of Metallurgy and
Mining Engineering

Tustison, Randal W., Research Assistant, Department of Metallurgy and
Mining Engineering

Tyner, Craig E., NSF Fellow, Department of Chemistry

Watson, James, Research Assistant, Department of Physics

Wilken, Theodore R., Research Assistant, Department of Metallurgy and
Mining Engineering (Term 1/22/76)

Yost, Gerald H., Research Assistant, Department of Ceramic Engineering

Zaluzec, Nestor J., Research Assistant, Department of Metallurgy and
Mining Engineering

Zapp, Philip E., Research Assistant, Department of Metallurgy and
Mining Engineering

Professional Staff**Materials Research Laboratory**

Baker, Judith A., B.A., Research Chemist
Blattner, Richard J., M.S., Research Chemist
Evans, Charles A. Jr., Ph.D., Senior Research Chemist
Metze, Virginia C., Research Computer Programmer
Ward, Ian D., Research Metallurgist
Williams, Peter, Ph.D., Research Chemist
Woodhouse, John B. B.A., Research Microprobe Analyst

PUBLICATIONS

(Calendar Year 1975)

There were 40 ERDA-supported publications for the Calendar Year 1975. In addition, there were 30 papers in process of publication.

ED-02-01-01-0 Structure of Materials

Paul A. Beck and C. P. Flynn, "Interpretation of the Susceptibility of Paramagnetic Nickel," *Solid State Commun.* 18, 127-130 (1975).

T. P. Darby and C. M. Wayman, "Growth of Gold Thin Film Dendrites on Graphite Substrates," *J. Cryst. Growth* 29, 98-108 (1975).

T. P. Darby and C. M. Wayman, "Nucleation and Growth of Gold Films on Graphite I: Effects of Substrate Condition and Evaporation Rate," *J. Cryst. Growth* 28, 41-52 (1975).

A. Mukhopadhyay, R. D. Shull, and Paul A. Beck, "Relaxation and Magnetic Clusters in Micromagnetic Cu-Mn Alloys," *J. Less Common Metals* 43, 69-82 (1975).

K. Otsuka and C. M. Wayman, "On the Shape Memory Effect in Internally Faulted Martensites," *Scripta Met.* 9, 1017-1022 (1975).

R. D. Shull and Paul A. Beck, "Micromagnetic to Ferromagnetic Transition in Cr-Fe Alloys," *AIP Conf. Proc.* 24, 95-96 (1975).

H. C. Tong and C. M. Wayman, "Thermodynamic Considerations of 'Solid State Engines' Based on Thermoelastic Martensitic Transformations and the Shape Memory Effect," *Met. Trans.* 6A, 29-32 (1975).

H. C. Tong and C. M. Wayman, "Thermodynamics of Thermoelastic Martensitic Transformations," *Acta Metall.* 23, 209-215 (1975).

C. M. Wayman, "Deformation, Mechanisms and Other Characteristics of Shape Memory Alloys," Shape Memory Effects in Alloys, edited by J. Perkins (Plenum Pub. Co., New York, 1975), pp. 1-28.

C. M. Wayman, "Shear Transformations and Microstructure," *Metallography* 8, 105-130 (1975).

C. M. Wayman and T. P. Darby, "Nucleation and Growth of Gold Films on Graphite II: The Effect of Substrate Temperature," *J. Cryst. Growth* 28, 53-67 (1975).

Lance Breger, Marvin Johnson, and Wendell Williams "Piezoelectric Response of Inorganic and Biological Materials Subjected to Inhomogeneous Stress," *J. Appl. Phys.* (submitted to).

Dwight R. Jennison and A. Barry Kunz, "Degree of Ionicity in Crystalline NaF, NaCl, SrF₂ and SrCl₂ and Found by Local Orbitals Hartree-Fock," Phys. Rev. (submitted to).

J. Jonas, T. DeFries, and D. J. Wilbur, "Molecular Motions in Compressed Liquid Water," J. Chem. Phys. (in press).

S. B. Kulkarni and W. S. Williams, "Dislocation Velocities and Electronic Doping in Silicon," J. Appl. Phys. (submitted to).

J. W. Linowski, Nan-I Liu and J. Jonas, "The Effect of Density and Temperature on the Hydroxyl Proton Chemical Shift in Liquid Ethanol," J. Magnetic Resonance (in press).

K. Otsuka and C. M. Wayman, "Pseudoelasticity and Stress-Induced Martensitic Transformations," Reviews on the Deformation Behavior of Materials (accepted).

ED-02-01-02-0 Mechanical Properties

H. K. Birnbaum and R. Wadley, "Hydrogen Embrittlement of Molybdenum," Scripta Met. 9, 1113-1116 (1975).

D. G. Chakrapani and E. N. Pugh, "The Transgranular SCC of a Mg-Al Alloy: Crystallographic, Fractographic and Acoustic-Emission Studies," Metall. Transactions 6A, 1155-1163 (1975).

D. G. Chakrapani and E. N. Pugh, "On the Fractography of Transgranular Stress-Corrosion Failures in a Mg-Al Alloy," Corrosion 31, 247-252 (1975).

Hamish L. Fraser and Ian P. Jones, "A Note on the Increase in Usable Foil Thickness in Scanning Transmission Electron Microscopy," Phil Mag. 31, 225-228 (1975).

H. L. Fraser, N. J. Zaluzec, J. B. Woodhouse, and L. B. Sis, "On the Feasibility of Quantitative Microchemical Analysis of Thin Metal Foils," 33rd Annual Proceedings Electron Microscopy Society, G. W. Bailey, ed. (Las Vegas, Nevada 1975) pp. 106-107.

Philippe Lecocq and Charles Wert, "Equilibrium in Hydride Formation in Tantalum," Thin Solid Films 25, 77-84 (1975).

R. F. Mattas and H. K. Birnbaum, "Isotope Effects on the Motion of O-H Clusters in Nb," Acta Metall. 23, 973-977 (1975).

M. Metzger, "Intergranular Corrosion of Single Phase Aluminum as Pitting Phenomenon," Journal de Physique 10, C4-387-393 (1975).

J. L. Nelson and E. N. Pugh, "The Occurrence of Transgranular Cleavage-Like Fracture in an Al-Zn-Mg Alloy During Tensile," Metall. Trans. 6A, 1459-1460 (1975).

M. F. Bluem and H. K. Birnbaum, "Determination of the Thermally Activated Deformation Parameters in Nb and Nb-N Alloys," Proceedings Int'l. Conf. on the Strength of Metals, France, 1976 (to be published).

D. G. Chakrapani, G. H. Koch, and E. N. Pugh, "On the Mechanism of SCC in a Mg-Al Alloy," Proceedings Sixth International Congress on Metallic Corrosion, Australia, 1975 (to be published).

D. G. Chakrapani and E. N. Pugh, "Hydrogen Embrittlement in a Mg-Al Alloy," Metall. Trans. (accepted).

H. Gabel, J. A. Beavers, J. B. Woodhouse, and E. N. Pugh, "The Structure and Composition of Thick Tarnish Films on Alpha-Phase Copper Alloys," Corrosion (accepted).

M. L. Grossbeck, Peter Williams, Charles A. Evans, Jr., and H. K. Birnbaum, "Application of Ion Probe Analysis to Studies of Hydrogen Behavior in Solids," Phys. Status Solidi A (in press).

Peter Williams, Charles A. Evans, Jr., Martin L. Grossbeck, and Howard K. Birnbaum, "Ion Microprobe Analysis for Niobium Hydride in Hydrogen-Embrittled Niobium," Anal. Chem. (in press).

ED-02-01-03-0 Physical Properties

T. J. Rowland, "A ^{14}N Nuclear Relaxation Study of Hydrogen Bonding in Diethylamine-Alcohol Solutions," J. Chem. Phys. **63**, 608-612 (1975).

T. J. Rowland and A. C. Yen, "A Study of Precipitation Using Nuclear Magnetic Resonance: Cu-2 wt.% Be," Acta Metall. (in press).

ED-02-02-02-0 Experimental Research

V. M. Cheng, P. C. Allen, and D. Lazarus, "Pressure Coefficient of Thermoelectric Power of Platinum/Platinum-10% Rhodium and Chromel/Alumel Thermocouples," Appl. Phys. Lett. **26**, 6-7 (1975).

V. M. Cheng, W. B. Daniels, and R. K. Crawford, "Melting Parameters of Methane and Nitrogen from 0-10 Kilobars," Phys. Rev. **B11**, 3972-3975 (1975).

R. K. Crawford, W. B. Daniels, and V. M. Cheng, "Melting and Its Relation to Molecular Orientations in the Fluid and Solid Phases of N_2 and CH_4 ," Phys. Rev. **A12**, 1690-1696 (1975).

H. G. Drickamer, "Exploratory Research at High Pressure," Materials Under Pressure, edited by T. Hirone (Maruzen Press Co., Tokyo, 1975), pp. 1-35.

H. G. Drickamer, "High Pressure Studies of Electronic Structure in Solids," International Review of Science - Inorganic Chemistry, Vol. 10, Solid State Chemistry, edited by L. E. J. Roberts (Butterworths, London, 1975), pp. 1-33.

H. G. Drickamer, "The Effect of Pressure on the Electronic States of Organic Solids," Proceedings of International Conference on Organic Synthesis, Belgium, 1974. Pure and Applied Chem. 43, 379-399 (1975).

J. A. Garber and A. V. Granato, "Fourth-Order Elastic Constants and the Temperature Dependence of Second-Order Elastic Constants in Cubic Materials," Phys. Rev. B11, 3998-4007 (1975)

J. A. Garber and A. V. Granato, "Theory of the Temperature Dependence of Second-Order Elastic Constants in Cubic Materials," Phys. Rev. B11, 3990-3997 (1975).

H. M. Gilder and D. Lazarus, "Role of Vacancy Anharmonicity on Non-Arrhenius Diffusional Behavior," Phys. Rev. B11, 4916-4926 (1975).

A. V. Granato, "Ultrasonic Studies of Mechanical Strength," Ultrasonics Symposium Proceedings IEEE Cat. #75 CHO 994-4SU (1975).

R. D. Isaac and R. B. Schwartz, "A Simple Persistent Switch for Superconducting Solenoids," Rev. Sci. Instrum. 46, 638 (1975).

Joan L. Mitchell and David Lazarus, "Effect of Heterovalent Impurities Codiffusing with Monovalent Tracers in Ionic Crystals," Phys. Rev. B12, 734-752 (1975).

R. B. Schwartz and A. V. Granato, "Measurement of the Force-Distance Profile for the Interaction Between a Dislocation and a Point Defect," Phys. Rev. Lett. 34, 1174-1177 (1975).

Charles P. Slichter, "Some Scientific Contribution of Herbert S. Gutowsky," J. Magnetic Resonance 17, 274-280 (1975).

K. D. Swartz, W. Bensch, and A. V. Granato, "The Second-, Third-, and Fourth-Order Elastic Constants of Beta Brass," Phys. Rev. B12, 2125-2131 (1975).

W. F. Weston and A. V. Granato, "Cubic and Hexagonal Single-Crystal Elastic Constants of a Cobalt-Nickel Alloy," Phys. Rev. B12, 5355-5362 (1975).

D. G. Wilson and H. G. Drickamer, "High Pressure Studies on Spiropyrans," J. Chem. Phys. 63, 3649-3655 (1975).

James B. Boyce and Charles P. Slichter, "Conduction-Electron Spin Density Around Fe Impurities in Cu Above and Below the Kondo Temperatures," Phys. Rev. (submitted to).

J. B. Boyce and C. P. Slichter, "Determination of the Energy Level Parameters and Crystal Field Splitting for Fe in Cu," Proceedings Conference on Magnetism and Magnetic Materials, Philadelphia, Pa., 1975 (to be published).

R. K. Crawford, W. F. Lewis, and W. B. Daniels, "Thermodynamics of Solid Argon at High Temperatures," Solid State Phys. C (to be published).

W. D. Drotning and H. G. Drickamer, "High Pressure Optical Studies of Doped Alkali Halides. I. Peak Shifts and Peak Shape Changes," Phys. Rev. (in press).

W. D. Drotning and H. G. Drickamer, "High Pressure Optical Studies of Doped Alkali Halides. II. Jahn Teller Effects," Phys. Rev. (in press).

W. D. Drotning and H. G. Drickamer, "High Pressure Optical Studies of Doped Alkali Halides. III. Rates of Electron Transfer Processes," Phys. Rev. (in press).

W. D. Drotning and H. G. Drickamer, "High Pressure Optical Studies of Doped Alkali Halides. IV. Mixed Crystals," Phys. Rev. (in press).

D. Follstaedt and C. P. Slichter, "An NMR Search for Charge Density Waves," Phys. Rev. (submitted to).

A. V. Granato, "Dislocation-Defect Interactions and Mechanical Properties of Crystals," Proceedings of International Conference on Radiation Damage in Solids, Gatlinburg, 1975 (to be published).

R. J. Nelson, N. Holonyak, Jr., W. R. Hitchens, D. Lazarus, and M. Altarelli, "Pressure Experiment Determination of the Direct-Indirect Transition in the Quaternary $\text{In}_{1-x}\text{Ga}_x\text{P}_{1-z}\text{As}_z$," Solid State Commun. (submitted to).

L. A. Schwalbe, "Equilibrium Vacancy Concentration Measurements in Solid Argon," Phys. Rev. B (to be published).

C. P. Slichter, "NMR Studies of the Kondo Effect Revisited," Proceedings Conference on Magnetism and Magnetic Materials, Philadelphia, Pa., 1975 (to be published).

C. E. Tyner, W. D. Drotning, and H. G. Drickamer, "Asymmetric Line Shapes of Localized Optical Excitations in Condensed Systems," J. Appl. Phys. (accepted).

ED-02-02-04-0 Particle-Solid Interactions

R. Berliner and J. S. Koehler, "Temperature Dependence of Transmission Proton Channeling in Ag," Phys. Rev. B12, 3559-3574 (1975).

J. Koehler, "Decrease in the Void Growth Rate by Interstitial Trapping," J. Appl. Phys. 46, 2423-2428 (1975).

R. Berliner and J. A. Koehler, "The Analysis of Forward Scattering Channeling Data," Radiation Effects (accepted).

R. C. Birtcher and J. S. Koehler, "The Recovery of Lead After Electron Irradiation at 1.5 K," Phys. Rev. (accepted).

Masao Doyama and J. S. Koehler, "The Relation Between the Formation Energy of a Vacancy and the Nearest Neighbor Interactions in Pure Metals and Liquid Metals," *Acta Metallurgica* (accepted).

J. S. Koehler, "Interstitials in Metals," Proceedings Conference on Radiation Damage in Metals, Gatlinburg, 1975 (to be published).

Ph.D. DISSERTATIONS

(Calendar Year 1975)

Eleven Ph.D. Theses were completed and degrees granted with ERDA support for the Calendar Year 1975.

D. R. Aadsen (R. O. Simmons, Adviser), "Lattice Parameter and Thermal Expansion in Solid Methane," October 1975.

Joseph Gary Baldoni II (W. S. Williams, Adviser), "High Temperature Deformation Behavior of Cemented Carbide Cutting Tools," January 1975.

Robert Charles Birtcher (J. S. Koehler, Adviser), "The Recovery of Lead After Electron Irradiation at 1.5 K," May 1975.

D. G. Chakrapani (E. N. Pugh, Adviser), "Transgranular Stress-Corrosion Cracking of a Magnesium-Aluminum Alloy," May 1975.

S. Chakravorty (C. M. Wayman, Adviser), "Crystallography of the Thermoelastic Martensitic Transformation in Ni-Al Alloys," October 1975.

W. D. Drotning (H. G. Drickamer, Adviser), "Luminescence of Impurity-Activated Alkali Halides Under High Pressure," October 1975.

David Martin Follstaedt (C. P. Slichter, Adviser), "A Nuclear Magnetic Resonance Study of Dilute Copper-Vanadium Alloys," January 1975.

Subhash B. Kulkarni (W. S. Williams, Adviser), "Velocities of Screw and 60°-Dislocations in Intrinsic and Extrinsic Silicon," October 1975.

David Thomas Read (A. V. Granato, Adviser), "Bias Stress Detection of Dislocation Resonance in Lead," May 1975.

D. Shah (C. J. Altstetter, Adviser), "Deformation of Vanadium Containing Dispersed $V_{16}N$ Particles," October 1975.

D. G. Wilson (H. G. Drickamer, Adviser), "Photochromic Studies of Spiropyrans," May 1975.

M.S. DISSERTATIONS

(Calendar Year 1975)

Eight M.S. theses were completed and degrees granted with ERDA support for the Calendar Year 1975.

M. Cassidy (C. M. Wayman, Adviser), "An Electron Microscopy Study of the Substructure of β -Hydride in Vanadium," May 1975.

E. N. Hockert (H. G. Drickamer, Adviser), "The Effect of Pressure on the Electronic Spectra of Some Salicylikineaniline," May 1975.

G. L. House (H. G. Drickamer, Adviser), "Effects of High Pressure on the Luminescence of Zinc Sulfide Phosphors," May 1975.

Scott E. Hughes (H. L. Fraser, Adviser), "A Preliminary Study of the Morphology of Hydride Precipitation in Tantalum," October 1975.

R. W. Lewis (C. A. Wert, Adviser), "The Solubility of Hydrogen in Vanadium," August 1975.

James G. Sheltens, (M. Metzger, Adviser), "Scanning Electron Microscope Study of Pitting on Aluminum in Sulfuric Acid Containing Chloride," 1975.

C. E. Tyner (H. G. Drickamer, Adviser), "Effects of Pressure on Oxygen Dominated Phosphors," May 1975.

T. Wilken (C. A. Wert, Adviser), "The Morphological Structure Produced During Reduction of Blue Tungsten Oxide to Tungsten Metal," May 1975.