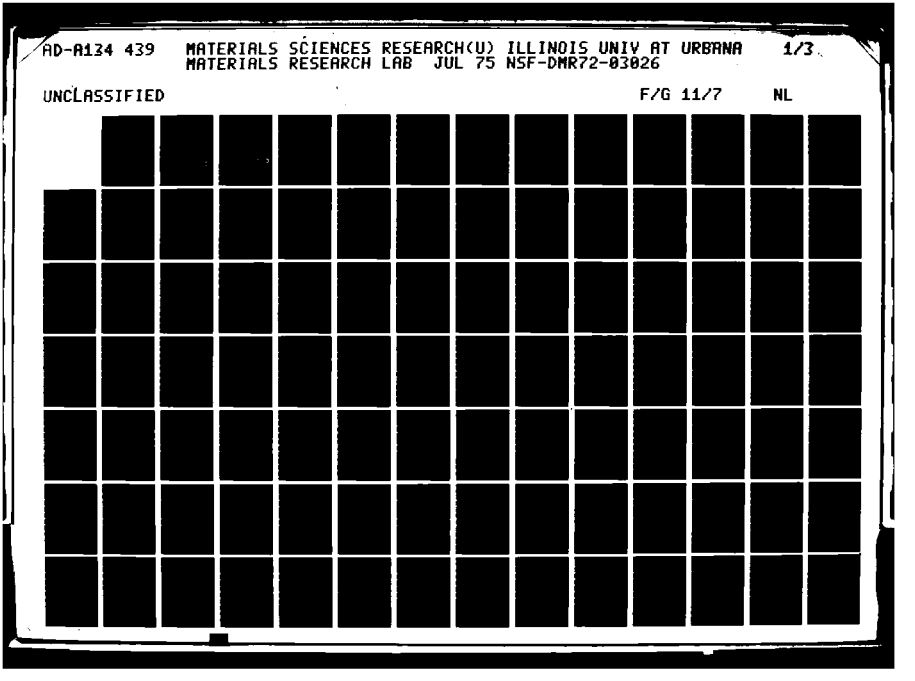
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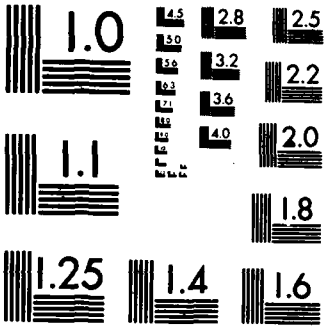

ANNUAL TECHNICAL REPORT

1974 - 1975

(July 1, 1974 thru June 30, 1975)

on

Materials Sciences Research

Submitted to the

NATIONAL SCIENCE FOUNDATION

DMR-72-03026

by the

MATERIALS RESEARCH LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

JULY 1975

This report lists the research output of all Materials Research Laboratory Project Principal Investigators. The research reported has been supported by the National Science Foundation, the Advanced Research Projects Agency, the U.S. Energy Research & Development Administration, the U.S. Office of Naval Research, the U.S. Air Force Office of Scientific Research, and the U.S. Army Research Office.

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INTRODUCTION

The Materials Research Laboratory of the University of Illinois was established in June, 1962, as an interdepartmental and interdisciplinary laboratory of the College of Engineering. The following departments of the University participate in its operation:

Department of Ceramic Engineering
Department of Chemistry and Chemical Engineering
Department of Electrical Engineering
Department of Geology
Department of Metallurgy and Mining Engineering
Department of Physics

The administration of the Laboratory is the responsibility of an Administrative Staff and a Steering Committee. The Administrative Staff of the Laboratory is:

Robert J. Maurer, Professor of Physics, Director
John Stanley, Business Manager

The Steering Committee of the Laboratory is:

C. J. Altstetter, Professor of Physical Metallurgy; Acting Head, Department of Metallurgy and Mining Engineering
H. G. Drickamer, Professor of Chemical Engineering and of Physical Chemistry
A. L. Friedberg, Professor of Ceramic Engineering; Head, Department of Ceramic Engineering
N. Holonyak, Jr., Professor of Electrical Engineering
R. O. Simmons, Professor of Physics; Head, Department of Physics
R. J. Maurer, Professor of Physics (ex-officio)

In 1973, an External Advisory Committee was appointed to advise the Director and Steering Committee. The members of the External Advisory Committee are:

J. E. Burke, General Electric Company
W. D. Compton, Ford Motor Company
M. Nevitt, Argonne National Laboratory
A. Overhauser, Purdue University
R. Oriani, U. S. Steel Corporation (Chairman)
C. A. Swenson, Iowa State University

An Internal Advisory Committee also consults with the Steering Committee concerning the Laboratory program and procedures. The present membership of this committee is:

J. Dow, Associate Professor of Physics
C. Flynn, Professor of Physics
H. Fraser, Assistant Professor of Metallurgical Engineering
J. Holder, Assistant Professor of Geology
J. Jonas, Professor of Chemistry
A. Kunz, Associate Professor of Physics
E. Pugh, Professor of Metallurgical Engineering
M. Salamon, Professor of Physics
G. Wirtz, Associate Professor of Ceramic Engineering

Primary support for the Laboratory is derived from contracts and grants of the National Science Foundation, the Energy Research and Development Administration, the Advanced Research Projects Agency of the Department of Defense, and the State of Illinois.

The scientific staff of the Laboratory is selected by the Steering Committee after review of proposals submitted by faculty members of the University. Proposals for renewal of research support are submitted annually; new proposals may be submitted at any time.

The numbers of senior faculty members whose research received direct financial support from Laboratory funds derived from contracts or grants with each of the supporting agencies, the number of postdoctoral research associates and graduate student research assistants whose stipends and research was supported by each agency are given in the following table:

Agency	Faculty	Postdoctorals	Graduate Students
NSF	21	11	45
ERDA	17	9	49
ARPA	6	7	20
Other		6	17
Total	44	33	131

Nine professional staff members of the Laboratory are employed in the Chemical Analytical Facility and Microstructure Facility.

Twenty-five nonacademic staff members are employed in administrative, clerical, and technical positions of the business office, machine shop, and facilities.

New Projects

Frederick C. Brown, Professor of Physics
Photoemission from the Layer Compounds with the Use of Synchrotron Radiation
Supported by the National Science Foundation

Jiri Jonas, Professor of Chemistry
Harry Drickamer, Professor of Chemical Engineering and Chemistry
Dynamic Structure of Supercritical Dense Water and Aqueous Electrolyte Solutions
Supported by the U.S. Energy Research and Development Administration

Terminated Projects

None

Visiting Staff Members

Dr. S. C. Jain, Director of Research and Training, Defense Research and Development Organization, Ministry of Defense, New Delhi, India, is a Visiting Professor of Physics, May 1 through October 31, 1975.

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

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

V. Malnev, Kiev State University, USSR, was a IREX Soviet Scholar in the Department of Physics from September 1974 through May 1975 and worked with A. Barry Kunz.

K. Otsuka, Institute of Scientific and Industrial Research, Osaka University, Osaka, Japan, is a Visiting Research Associate Professor in the Department of Metallurgy, working with C. M. Wayman's group.

Dr. Michael Skibowski, University of München, Germany, is a Visiting Associate Professor of Physics from January 1, 1975 through August 31, 1975, working with F. C. Brown.

Seminars by Visitors

Dr. Sudraud, Laboratorie des Solid State, University of Paris, Orsay, "Field Desorption of Organic Liquids," August 14-16, 1974.

Professor H. Wollenberger, University of Aachen, Germany, "Defect Production by Electron Damage in Gold," August 27, 1974.

Dr. H. J. Liebl, Max Planck Institut für Plasmaphysik, Garching bei Munchen, W. Germany, "Ion Microprobes and the Mattauch-Herzog Geometry," September 19, 1974

Dr. Ronald Linz, Solid State Science, Argonne National Laboratory, "Dislocation Lattice Resistivity in Concentrated Alloys," September 17, 1974.

Professor L. P. Gor'kov, L. D. Landau Institute of Theoretical Physics, Moscow, USSR, "Toward a Theory of Superconductivity in the A-15 Compounds," November 1-4, 1974.

Dr. Elliot R. Bernstein, Department of Chemistry, Princeton University, "Interactions in Molecular Crystals: Spectroscopic Studies of Transition Metal Hexafluorides," November 21, 1974.

Dr. Sonnenberg, Jülich, Germany, "Recovery of Electron Irradiated Pb and Cu," November 14, 1974.

Dr. Peter de Chatel, Physical Science Laboratory, University of Amsterdam, "Charge Transfer in Alloys," December 12, 1974.

Dr. Hartmut Wiedersich, Argonne National Laboratory, "High Temperature Radiation Damage," March 5, 1975.

Professor Tetsuro Suzuki, Yokohama City University, Yokohama, Japan, "Martensitic Transformations and Lattice Instabilities," April 8, 1975.

Dr. P. A. Egelstaff, University of Guelph, Ontario, Canada, "Three-Body Effects in Simple Fluids," April 9, 1975.

Professor G. Leibfried, Oak Ridge National Laboratory, "Polarization of Point Defects," April 24-26, 1975.

Professor G. Fritsch, Technical University of Munich, "Measurements of Physical Properties of Sodium Near its Melting Temperature," June 16, 1975.

Other Visitors

Professor Masao Shimizu, Nagoya University, Japan, visited the Laboratory and consulted with P. Beck, about invar problems, June 24-25, 1974.

Dr. K. Bönig, University of München, Germany, visited the Laboratory and had research discussions with J. S. Koehler, June 28 - July 1, 1974.

Professor Milton Ferreira de Souza, Universidade De Sao Paulo, Sao Carlos, Brazil, visited the Laboratory and consulted concerning Fourier Transform Spectroscopy, July 18-20, 1974.

Professor T. Hehenkamp, University of Göttingen, Germany, visited the Laboratory and consulted with D. Lazarus, August 25, 1974.

Professor Etienne Guyon, Universite de Paris, Orsay, France, visited the Laboratory and had discussions with W. McMillan, September 3, 1974.

Professor J. Weertman, Department of Materials Sci[illegible], Northwestern University, Evanston, consulted with J. Holder at [illegible]ice research evaluation, October 31, 1974.

Dr. Sonnenberg, Jülich, Germany, visited the Labor[illegible]ry and gave a talk on "Recovery of Electron Irradiated Pb and Cu," Noven[illegible], 1974.

Dr. Peter de Chatel, Physical Science Laboratory, University of Amsterdam, visited the Laboratory and gave a talk on "Charge Transfer in Alloys," December 12, 1974.

Professor Humphrey J. Maris, Department of Physics, Brown University, visited the Laboratory and consulted on liquid helium research, February 20, 1975.

Professor K. Shimizu, Institute of Science & 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.

Dr. A. Marshall Stoneham, Harwell, England, visited the Laboratory and consulted with C. P. Flynn, May 28-31, 1975.

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

Dr. S. Radhakrishna, Center for Chemical Physics, London, Ontario, Canada, visited the Laboratory and consulted with M. V. Klein, May 20, 1975.

Honors and Awards

BARDEEN, J., Departments of Electrical Engineering and Physics
Elected to National Inventors Hall of Fame, 1974
D. Sci. (Hon.), University of Michigan, 1974

BECK, P. A., Department of Metallurgy and Mining Engineering
Honorary Member, Hungarian Physical Society, 1974
Wakefield Recognition Award, University of Illinois, 1975

BERGERON, C. G., Department of Ceramic Engineering
Everitt Undergraduate Teaching Excellence Award, University of Illinois, 1975

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

HOLONYAK, N., Jr., Department of Electrical Engineering
John Scott Award, 1975
Invited guest of the USSR Academy of Science; visited and gave seminar presentations at the Lebedev Institute (FIAN, Moscow), the Physico - Technical Institute (Leningrad), and the Tbilisi Laboratory of the USSR Academy, June 1975

PINES, D., Department of Physics
Guilio Racah Memorial Lecturer, Hebrew Univesity, 1974

SAH, C. T., Departments of Electrical Engineering and of Physics
Honorary Doctorate, Catholic University, Louvain, Belgium, 1975

SALAMON, M. B., Department of Physics
Senior U. S. Scientist Award (U.S. Special Program for Cooperative West German-U.S. Scientific Research), 1974-75

SLICHTER, C. P., Department of Physics
Wakefield Recognition Award, University of Illinois, 1975

Leaves

ANDERSON, A. C., Department of Physics
I Sem 1974-75
University of Illinois

BIRNBAUM, H. K., Department of Metallurgy and Mining Engineering
II Sem 1974-75
AERE, Harwell, England

SALAMON, M., Department of Physics
1974-75
Technische Universitat München, West Germany

WERT, C. A., Department of Metallurgy and Mining Engineering
1974-75
Head, Metallurgy and Materials Section, Division of Materials Research, National Science Foundation, Washington, D. C.

WILLIAMS, W. S., Departments of Ceramic Engineering and Physics
1974-75
Task Coordinator for Energy-Related General Research, Division of Materials Research, National Science Foundation, Washington, D. C.

Retired

BARDEEN, John, Departments of Electrical Engineering and Physics
February 1975

Central Facilities

The major central facilities serve general needs of the research program. Minor central facilities serve the more specialized interests of particular groups but are available to all who have need of them.

A. Major Facilities

1. The Chemical Analytical Laboratory

Instrumentation includes an AEI MS-7 mass spectrograph, an AEI IM20 ion microprobe, a Baird 3 meter emission spectrograph, a Jarrell Ash flame emission - atomic absorption spectrophotometer, and equipment for polarographic and wet chemistry analysis.

Supervision of the facility is by Associate Professor Charles A. Evans, Senior Research Chemist of the Materials Research Laboratory. He is assisted by four professional staff members:

Mr. Peter Williams, Ph.D., Research Chemist

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

Mrs. J. Baker, B.A., Research Chemist

Mrs. C. Silber, B.A., Assistant Research Chemist

Associate Professor Evans of the Department of Chemistry and Research Associate Professor Giovanni DePasquali of the Department of Physics are the MRL faculty committee for the facility. During fiscal year 1975, approximately 75% of the facility's effort was given to service analyses and 25% was spent on instrumentation and technique development.

Instrumentation and technique development during the past year has concentrated on the ion microprobe. An electronic aperture for depth profiling, improved secondary ion optics, and improved primary beam optics to reduce spot size were designed and installed. Significant improvement was made in the duoplasmatron primary ion source for better stability and

negative ion production. Considerable effort was given in cooperation with the Microstructure Facility to development of Auger techniques.

After July 1, 1975 the services of the Chemical Analytical Laboratory will be made available to other Laboratories of the NSF-MRL system.

2. The Microstructure Facility

Instrumentation includes a JSEM-200 kilovolt electron microscope with tilting and cold stages and STEM scanning attachment, a JSM-03 scanning electron microscope, an ARL EMX electron probe microanalyzer, a Physical Electronics Model 545 scanning Auger microprobe, an ion milling machine, two X-ray stations with diffractometer and Laue capabilities, a metallographic laboratory equipped with grinding and polishing wheels and a Zeiss metallograph.

The facility is supervised by a professional staff member, Mr. John Woodhouse, B.A., Research Microprobe Analyst, with the assistance of Mr. Ian Ward, Research Metallurgist. C. Wert, H. Fraser and Mr. J. Woodhouse compose the facility committee. Mr. Woodhouse and Mr. Ward give instruction and assistance to the students and faculty who use the facility.

3. The Computer Facility

A Xerox Sigma 5 computer system with 96,000 words of electronic memory and over 100 megabytes of magnetic disc storage is available to all members of the Laboratory and has over 150 consistent users. Peripheral equipment includes a card reader, magnetic and paper tape drives, a printer and a CalComp plotter. There is a time sharing system of sixteen lines with ASR33 teletypes placed throughout the MRL building. Timesharing and batch jobs run concurrently. Three telephone lines interface the computer to permit on line processing of data from apparatus in laboratories.

Supervision is by a professional staff member, Mrs. V. Metze, Research Computer Programmer, who is assisted by eight part-time student operators and a laboratory committee composed of A.B. Kunz, H. Stapleton, and Mrs. V. Metze.

4. The Machine Shop

A well-equipped, conventional machine shop, which includes an area and machines for faculty and student use, employs nine machinists under the supervision of Mr. Wayne Craig. H. Stapleton and Mr. F. Wise, Technical Services Supervisor, are the Laboratory Shop Committee.

5. The Storeroom

The Laboratory maintains a storeroom for the sale of scientific, electronic and metals stock items. Mr. Carroll Sarver, Storekeeper, operates the storeroom with two assistants. A laboratory committee consisting of A. Anderson and Mr. John Stanley, Laboratory Business Manager, supervises operations.

B. Minor Facilities

1. The Optical Laboratory

Beckmann IR-9 and IR-11 infrared spectrophotometers, an infrared Fourier interferometer, Cary 14R and 15 ultraviolet spectrophotometers, and a Spex 1401 monochromator with lasers for Raman spectroscopy are supervised by M. Klein.

2. The Mechanical Test Laboratory

A model 810 Materials Testing System is supervised by Carl Altstetter.

3. The High Temperature Laboratory

Two vacuum furnaces, a dilatometer, and several high temperature furnaces and ovens are supervised by S. Brown of the Department of Ceramic Engineering.

4. The Toxic Materials Laboratory

A special hood, dry box, and plumbing facilities are housed in a room with its own ventilation system for preparative work on toxic inorganic compounds of thallium, lead, beryllium, etc. S. Brown supervises the use of the facilities which are of primary interest to the ceramists.

5. The Materials Preparation Laboratory

This facility is composed of two areas: one is equipped with two vacuum systems (10^{-6} and 10^{-11} Torr) and a zone refiner for preparation of pure niobium under the supervision of H. Birnbaum. The other area is eqipped for the synthesis and growth of one dimensional organic cryst als by G. Stucky and G. DePasquali.

6. The Accelerator Laboratory

This laboratory houses a 3 MeV Van de Graaff accelerator which is operated by two technicians under the direction of J. Koehler. Provision for electron and proton beams exists.

7. The Cryogenic Laboratory

This area contains fifteen cryostat stations with pumping lines, pumps, a helium recovery system and magnets for low temperature research. D. Ginsberg supervises the use of the facility and it is presently occupied by the low temperature groups of D. Ginsberg, J. Mochel, C. Satterthwaite and T. Brown.

SCIENTIFIC PROGRAM

The scientific program of the Laboratory is organized within six areas of concentration:

Degenerate Quantum Systems
Electron-Lattice Coupling
Disordered Materials
Surfaces, Interfaces, Small Particles and Catalysis
Mechanical Properties of Materials
Semiconductor Materials and Devices

This section of the Annual Technical Report contains information concerning the research programs of faculty members which received direct financial support from the Laboratory in fiscal year 1975. As a result of interaction and collaboration between members of the Laboratory, their research programs commonly contribute to more than one area of concentration. Examination of the individual reports will reveal areas of activity of each investigator other than that of the primary listing.

1. Degenerate Quantum Systems

Theory of the Condensed State of Matter

Principal Investigator: John Bardeen, Ph.D.
Professor of Physics and of Electrical Engineering;
Member, Center for Advanced Study

Supporting Agency: National Science Foundation

Senior Staff: John Bardeen, Professor
Gordon Baym, Professor
Christopher Pethick, Professor
David Pines, Professor
Michael Wortis, Professor
Carl O. Almbladh, Research Associate (Begin 12/21/74)
Partha Bhattacharyya, Research Associate
Roger A. Smith, Research Associate (Until 12/21/74)

Junior Staff: Charles Aldrich III, Research Assistant (Until 10/15/74)
James W. Bray, Research Assistant (Until 8/20/74)
Tan-Hua Yu, Research Assistant (Begin 5/21/75)

Objective: To investigate those aspects of theoretical solid state and low temperature physics which are concerned with surface physics, conduction in pseudo-one-dimensional solids, optical and photoconducting properties of insulators and semiconductors, superconductors, and superfluid phases of ^{3}He and ^{4}He. Much of the theoretical research is parallel with and supports experimental investigations.

Approach: Many-body theoretical concepts and techniques are used and computer calculations employed.

Progress: (01 07 74 - 30 06 75) Theoretical work has been done to investigate the possibility of enhancing the superconducting transition temperature at the interface between a thin metallic film and an appropriate semiconductor. It is hoped to decrease the Coulomb repulsion of metallic electrons near the Fermi surface by virtual creation of electron-hole pairs in the semiconductor. Methods for estimating the dielectric

response, $\epsilon(q,\omega)$, of a semiconductor for general q and ω are given in the Ph.D. thesis of David W. Allender, finished in October, 1974 (under Professor J. Bardeen). The theory indicates that conditions for observing the effect are exacting although not impossible to attain. Experiments have so far been negative.

A semi-phenomenological theory has been developed to estimate the excess conductivity from fluctuations of charge density waves in pseudo-one-dimensional systems just above the Peierls transition from a metallic to an insulating state. Methods for estimating the magnitude according to mean field theory are described in the Ph.D. thesis of J. W. Bray, completed in September, 1974. Experiments, including x-ray measurements, have confirmed the presence of charge density waves in TTF-TCNQ, indicating that this is the likely mechanism for conductivity enhancement in this system. Theoretical assistance has been given to those doing experimental work in the area at Illinois (Salamon, Stucky, et al.)

Charles Aldrich, III completed his thesis (under Professor D. Pines) in September, 1974 on use of the coherent potential method in order to better understand the dispersion at small wave vector in liquid He II. The theory was successful in accounting for a change in sign of dispersion required by experiment.

P. Bhattacharyya and Professor C. J. Pethick in collaboration with H. Smith of the University of Copenhagen have calculated the viscosity, thermal conductivity and other transport properties of the newly found superfluid phases of ^{3}He. Results are in reasonable agreement with experiments of the Helsinki group.

In collaboration with Professor W. L. McMillan, work has been done on molecular theory of smectic C, B and H phases of liquid crystals.

Publications: (01 07 74 - 30 06 75)

Dipan K. Ghosh and P. Bhattacharyya
Applications of Coherent Potential Approximations to Ni-Rich Ni-Cu Alloys
Physical Review B 11, 2642-2650 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026

C. J. Pethick, H. Smith, and P. Bhattacharyya
Viscosity and Thermal Conductivity of Superfluid ^{3}He: Low-Temperature Limit
Physical Review Letters 34, 643-646 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026

M. B. Salamon, J. W. Bray, G. DePasquali, R. A. Craven, G. Stucky, and A. Schultz
Thermal Conductivity of Tetrathiofulvalinium-Tetracyanoquinodimethane (TTF-TCNQ) near the Metal-Insulator Transition
Physical Review B 11, 619-622 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026

P. B. Visscher
High Temperature Thermodynamics of the Hubbard Model: An Exact Numerical Solution
Physical Review B 10, 932-942 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

P. B. Visscher
Phase Separation in the Hubbard Model at Zero Temperature
Physical Review B 10, 943-945 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

P. Bhattacharyya, C. J. Pethick, and H. Smith
Spin Relaxation in Superfluid ^{3}He
Physical Review Letters (Comments) (submitted to)
Supported by the National Science Foundation under Grant DMR-72-03026

P. Bhattacharyya, C. J. Pethick, and H. Smith
Transport Phenomena in Superfluid ^{3}He Near the Transition Temperature
Fourteenth International Conference on Low Temperature Physics, Finland, 1975 (submitted to)
Supported by the National Science Foundation under Grant DMR-72-03026

A. Barry Kunz and Daniel J. Mickish
Electronic Structure of LiH and NaH
Physical Review (submitted to)
Supported by the National Science Foundation under Grant DMR-72-03026, by the Army Research Office under Contract DA-HC04-69-C0007, and by the Aerospace Research Lab under Contract F-33615-72-C-1506

C. J. Pethick, H. Smith, and P. Bhattacharyya
Viscosity of Superfluid Liquid ^{3}He near the Transition Temperature
Physical Review Letters (submitted to)
Supported by the National Science Foundation under Grant DMR-72-03026

M.S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses: (01 07 74 - 30 06 75)

Charles Henry Aldrich, III (D. Pines, Adviser)
Polarization Potentials and Elementary Excitations in Strongly Interacting Quantum Liquids
October 1974
Supported by the National Science Foundation under Grant DMR-72-03026 and by the Army Research Office under Contract DAHC-04-74C-005

David William Allender (J. Bardeen, Adviser)
Model for an Exciton Mechanism of Superconductivity in Planar Geometry
January 1975
Supported by the National Science Foundation under Grant DMR-72-03026 and by the Army Research Office under Contract DA-HC04-74-005

James William Bray (J. Bardeen, Adviser)
Fluctuation Conductivity from Charge Density Waves in Pseudo-One-Dimensional Systems
October 1974
Supported by the National Science Foundation under Grant GH-33634 and by the Advanced Research Projects Agency under Contract SD-131

Jared Logan Johnson (J. Bardeen, Adviser)
Current Flow in Inhomogeneous Superconductors
October 1974
Supported by the Advanced Research Projects Agency, by the Army Research Office, and by a National Science Foundation Traineeship

Superconductors

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

Supporting Agency: National Science Foundation

Senior Staff: Donald M. Ginsberg, Professor
Patrick Tai, Research Associate

Junior Staff: Brian C. Gibson, Research Assistant
Jeffrey O. Willis, Research Assistant

Objectives: We are performing two different experiments. The purpose of the first one is to test experimentally the theory of Rusinov, Shiba, Nagi, and others of the interactions of electrons in superconductors with strongly perturbing magnetic impurities (3d magnetic impurities). The research is of fundamental importance, and is also relevant to the development of thin-film superconducting devices.

The purpose of our second experiment is to contribute to our understanding of the way in which heat is conducted by electrons in inhomogeneous superconductors.

Approach: For the first experiment, precision measurements are being made of the specific heat of superconducting film samples. An ac specific heat technique is used. The film is flash-evaporated to avoid precipitation of the impurities.

For the second experiment, films of indium alloyed with about 2% bismuth are cooled below the superconducting transition temperature and exposed to a dc magnetic field, oriented perpendicular to the sample's surface. Quantized magnetic vortices are formed, with associated variations in the superconducting order parameter. The thermal conductivity of the sample is then measured as a function of temperature

and magnetic field. The results will be interpreted with the aid of the theory of Caroli and Cyrot of the thermal conductivity in this type of situation.

Progress: (01 07 74 - 30 06 75) In the first experiment, we have put our equipment into operation. We have solved technical problems associated with preparing the samples, and we are obtaining our first significant data.

In the second experiment, we have modified a cryostat for the desired type of measurement, and have made our first samples and run them. We are now accumulating more data.

Two other projects have been concluded in the past year. In one of them, we have compared theoretical predictions with measurements of the superconducting transition temperature in alloys containing 3d magnetic impurities, and have published the results. They indicate the importance of electron orbital degeneracy in this problem. In the other project, we have measured the attenuation of a magnetic field by thin superconducting lead films, and have published the results. They agree well with a theoretical calculation which we have performed. The effect of strong electron-phonon coupling in lead was an important ingredient in the calculation.

Publications: (01 07 74 - 30 06 75)

D. M. Ginsberg
The Depression of the Superconducting Transition Temperature Caused by Iron-Group Magnetic Impurities
Physical Review (Comments and Addenda) 10, 4044-4045 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-37980

D. M. Ginsberg and B. J. Mrstik
Electronic Part of the Thermal Conductivity of a Thin, Superconducting Film Composed of Lead and Gadolinium
Low Temperature Physics LT 13, 767-771 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GP-28996

H. R. Kerchner and D. M. Ginsberg
Magnetic Field Attenuation by Thin Superconducting Lead Films
Physical Review B 10, 1916-1926 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-37980

M.S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses: (01 07 74 - 30 06 75)

Harold Richard Kerchner (D. M. Ginsberg, Adviser)
The Superconducting Penetration Depth in Thin Films of Lead
October 1974
Supported by the National Science Foundation under Grant DMR-72-03026

Properties of Materials at Very Low Temperatures

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

Supporting Agency: National Science Foundation

Senior Staff: Ansel C. Anderson, Professor
Stephen G. O'Hara, Research Associate (Term 12/12/74)
C. Lewis Reynolds, Jr., Research Associate (Begin 1/21/75)

Junior Staff: John H. Anderson, Research Assistant (Begin 1/6/75)
Roland G. Deptuch, Research Assistant (Until 1/5/75) and
Teaching Assistant (Begin 1/6/75)
James R. Matey, Research Assistant (Begin 3/16/75)
Emanuel P. Roth, Research Assistant (Summer 1975)
Gregory J. Sellers, Research Assistant (Term 10/10/74)
Terry L. Smith, Research Assistant (Begin 1/6/75) and
University Fellow
James L. Vorhaus, Research Assistant (Begin 1/6/75)
Mark P. Zaitlin, Research Assistant (Begin 3/16/75)

Objectives: (1) Experimental research on the transport, thermal and magnetic properties of pure materials and those containing impurities and lattice defects (helium, normal and superconducting metals, amorphous and crystalline dielectrics); (2) A basic understanding of materials and phenomena important to low temperature technology.

Approach: Low temperatures are used to take advantage of the simplifications that occur in the physics of transport processes and other properties at such temperatures, to study certain phenomena that occur only at low temperatures, and to provide as an experimental tool a source of very high frequency phonons.

Progress: (01 07 74 - 30 06 75)

(a) Heat Transfer Between Dissimilar Materials - If two materials, at least one of which is not a metal, are placed in intimate contact, a thermal impedance to heat flow (R_B) occurs at the interface. R_B becomes especially

large at low temperatures. We have shown that R_B between various metals and insulating materials (including liquid and solid ^3He and ^4He at very low temperatures) is accounted for very well by a semiclassical theory describing the interaction of phonons with the interface and with electrons and defects near the interface. The theory can also correctly account for the heat exchange within rather complicated and practical systems such as metal parts isolated by electrical insulation.

(b) Properties of Non-Crystalline Materials - The specific heat, thermal conductivity, and other properties of a vast class of amorphous materials are not understood and are the subject of vigorous research in several laboratories. We have shown experimentally that thermal transport is provided by phonons at temperatures up to at least 30 K, and probably at higher temperatures as well. We have shown that, contrary to the case with crystalline materials, phonons scatter specularly from abraided surfaces of amorphous materials. It has been demonstrated that glassy metals have a thermal conductivity similar to amorphous dielectrics, even though there had been some evidence suggesting that this would not be the case. We showed that the anomalous specific heat of glasses is not related to dissolved light gases, thus eliminating one more type of impurity from a list of possible candidates. Finally, we have shown that the currently popular tunneling-states model does a rather good job of describing the specific heat, the thermal conductivity between 0.01 and 30 K, and an empirical relationship between the specific heat and thermal conductivity. (This work was supported in part by NSF Grant GH-39135.)

Publications: (01 07 74 - 30 06 75)

A. C. Anderson
The Kapitza Resistance and Related Phenomena
Proceedings of the European Physical Society Topical Conference on Liquid and Solid Helium, Haifa, Israel, 1974
Supported by the National Science Foundation under Grant DMR-72-03026

A. C. Anderson and S. G. O'Hara
The Lattice Conductivity of Normal and Superconducting Niobium
Journal of Low Temperature Physics 15, 323-333 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

J. F. Folinsbee and A. C. Anderson
The Kapitza Resistance to a Variety of Metallic Surfaces Below 0.3 K
Journal of Low Temperature Physics 17, 409-424 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

S. G. O'Hara and A. C. Anderson
The Electronic Thermal Conductivity of Strained Aluminum Below 1 K
Physica Status Solidi B 67, 401-404 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026

S. G. O'Hara and A. C. Anderson
Resonant Scattering of Thermal Phonons by Dislocations in Superconducting Aluminum
Physical Review B 9, 3730-3734 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

S. G. O'Hara and A. C. Anderson
The Scattering of Thermal Phonons by Dislocations in Superconducting Lead and Tantalum
Physical Review B 10, 574-579 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

S. G. O'Hara and A. C. Anderson
Thermal Impedance Across Metallic and Superconducting Foils Below 1 K
Journal of Physics and Chemistry of Solids 36, 1677-1682 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

S. G. O'Hara, G. J. Sellers, and A. C. Anderson
The Influence of Hydrogen on the Thermal Conductivities of Superconducting Nb and Ta
Physical Review B 10, 2777-2781 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

G. J. Sellers and A. C. Anderson
Calorimetry Below 1 K: The Specific Heat of Copper
Review of Scientific Instruments 45, 1256-1259 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

G. J. Sellers, A. C. Anderson, and H. K. Birnbaum
The Anomalous Heat Capacities of Niobium and Tantalum Below 1 K
Physical Review B 10, 2771-2776 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026 and by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

G. J. Sellers, M. Paalanen, and A. C. Anderson
The Anomalous Heat Capacity of Superconducting Vanadium
Physical Review B 10, 1912-1915 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

J. L. Vorhaus and A. C. Anderson
The Low Temperature Specific Heat of Vitreous Silica Containing Hydrogen and Helium Solutes
Journal of Non-Crystalline Solids 17, 241 (1975)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39135

M. P. Zaitlin and A. C. Anderson
Thermal Conductivity of Borosilicate Glass
Physical Review Letters 33, 1158-1161 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39135

M. P. Zaitlin and A. C. Anderson
Thermal Conductivity of Deformed Germanium Below 1 K
Physical Review B 10, 580-581 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

J. R. Matey and A. C. Anderson
Thermal Conductivity of a Glassy Metal at Low Temperatures
Proceedings of the International Conference on Thermal Conductivity, Storrs, Connecticut, 1975 (submitted to)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39135

C. L. Reynolds and A. C. Anderson
Thermal Boundary Resistance to Non-Crystalline Dielectrics
Journal of Low Temperature Physics (submitted to)
Supported by the National Science Foundation under Grant DMR-72-03026

M. P. Zaitlin and A. C. Anderson
An Explanation for the Plateau in the Thermal Conductivity of Non-Crystalline Solids
Physica Status Solidi B (submitted to)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39135

M. P. Zaitlin and A. C. Anderson
Phonon Thermal Transport in Noncrystalline Materials
Physical Review (submitted to)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39135

M. P. Zaitlin, L. M. Scherr, and A. C. Anderson
On the Boundary Scattering of Phonons in Non-Crystalline Materials
Physical Review (submitted to)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39135

M.S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses: (01 07 74 - 30 06 75)

James Terwillegar Folinsbee (A. C. Anderson, Adviser)
The Kapitza Resistance at Metal-Helium Interfaces
October 1974
Supported by the National Science Foundation under Grant DMR-72-03026

Gregory Jude Sellers (A. C. Anderson, Adviser)
Low Temperature Anomalies in Niobium, Vanadium and Tantalum
October 1974
Supported by the National Science Foundation under Grant DMR-72-03026 and by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

Cooperative Phenomena at Low Temperatures

Principal Investigator: Jack M. Mochel, Ph.D.
Associate Professor of Physics

Supporting Agency: National Science Foundation

Senior Staff: Jack M. Mochel, Associate Professor

Junior Staff: Edward L. Griffin, Research Assistant
Daniel L. Rascoe, Research Assistant
James E. Rutledge, Research Assistant
John E. Smaardyk, Research Assistant
Lawrence N. Smith, Graduate Student (NSF, non-MRL)
Ted Washburn, Graduate Student (NSF, non-MRL)

Objectives: The understanding of thermodynamic stability in superconductors, especially in amorphous metals. This study will also include a general investigation of quench-condensed amorphous metals below 7 K. The effects of thermodynamic fluctuations on the superconducting state can be crucial in establishing high temperature superconductivity. In fact, such effects can be seen in some materials well above their superconducting transition temperature, even near the boiling point of liquid nitrogen.

A second objective of our research is the study of the physics of liquid surfaces, especially He^4 with and without He^3 impurities. The study of surfaces, liquid or solid, is often plagued with surface impurities. We have the unique ability, with the surface of He^4, to avoid these problems. In addition, such a study permits an experimental test of several theories of surfaces where quantum statistical mechanics in two dimensions is involved.

Finally, we are preparing to study how heat flows across a liquid-solid interface at low temperatures. At higher temperatures the problem of heat transfer is of great practical importance wherever cooling or heat

exchange is involved. At cryogenic temperatures the resistance to heat transfer becomes large and can be carefully studied.

Approach: To study the effect of thermodynamic fluctuations on amorphous metal superconductors we have chosen to study the heat capacity of thin films. This offers two advantages. First, many unique materials can be prepared and studied in-situ. The amorphous metals can be reproducibly condensed from a vapor on a substrate cooled below 4 K. Amorphous materials formed at higher temperatures can often be unstable or partially crystallized. Second, the effect of thermodynamic fluctuations on the superconducting state is enhanced in thin films, and can be more easily studied.

We have overcome the problem of small sample size for heat capacity measurements by using a non-adiabatic way of measuring heat capacity. This technique is a variation of the ac heat capacity technique which has been used successfully by several other groups within MRL. The rediscovery and success of this method is a direct result of the strong interplay between research programs within MRL.

To study the surface of He^4 in its two dimensional, superfluid state we have created a "two dimensional" resonant cavity. The desired amount of helium gas is diffused through the walls of a quartz capsule at room temperatures. At low temperatures this gas coats the inner surface of the capsule with a superfluid film a few atomic layers thick. This closed surface supports third sound waves. Since this capsule can be reused, accurate studies of Van der Waals force, superfluidity and thermodynamic fluctuations can be made. Using the same capsule, measured amounts of He^3 surface impurities can also be added. Below 1°K, He^3 will float on the

He^4 film. We have also placed capacitor plates within the walls of this capsule to monitor pressure.

To study heat flow across a solid-liquid interface we are generating monochromatic phonons in two different ways. We are using a double tunnel junction composed of three aluminum films separated by Al_2O_3 barriers. One junction serves as a generator, indirectly, of phonons and the second junction serves as a detector. By operating this system in a vacuum and then with liquid helium we can establish the phonon absorption at a particular temperature and frequency. A second approach we are beginning is to generate phonons at 70 GHz in a doped CaF_2 crystal using ESR. This technique promises to give high resolution results of the dispersion of phonons at a liquid-solid interface and also the behavior of these phonons in liquid helium.

Progress: (01 07 74 - 30 06 75) During the past year we have built, through the MRL shop, a combination cryostat and evaporator capable of quench condensing amorphous metal films on a cold substrate in an effective vacuum, during condensation, of better than 10^{-9} Torr. With this cryostat we can then study the heat capacity of such films down to 0.3 K.

We are studying presently the amorphous Ge-Noble metal system and the Sb-Bi system. We have achieved, through an interface to our Wang 720 calculator, a resolution of 3 parts in 10^5 of a total heat capacity of 0.1 erg/deg. We are presently measuring the fluctuation heat capacity of these systems.

The post analysis of these films is done through Auger spectrometry by Mr. Woodhouse in the Microstructure Facility.

For helium films, progress of three kinds, two basic and one practical, has been made.

First, we have demonstrated that the excitations from helium films less than 3 atomic layers thick are two dimensional and phonon like. This, in turn, means that there can be a state of two dimensional superfluidity. This conclusion has a direct bearing on the kind of theory that can be used for superfluids (limited long range order).

Second, the nature of these two dimensional excitations raises a basic question about the physics of the surface of liquid helium and perhaps any liquid. There is the puzzling absence of the thermally excited hydrodynamic surface excitations.

Finally, to do these measurements, we have had to develop a quartz capsule which not only contains the superfluid film but also allows, thru a flexing of its walls and a change in electrical capacitance, a measurement of pressure to a resolution of 10^{-5} Torr in-situ. The small size and stability of this device will make it useful for many other applications. The dust free Chemical Analytical Facility and cooperation of Professor C. Evans is essential to the assembly of these capsules.

A major result, in the study of phonon absorption at a liquid-solid interface is the demonstration that the presence of liquid He^4 has a large effect on the phonon and thus the quasi-particle life time within the junction. This, in turn, has also allowed us to extract the intrinsic life time of the superconducting excitations. We expect these observations to make a major contribution to the understanding of superconductivity. During the past we have also been constructing a dilution refrigerator within which we can study phonon radiation thru a surface below 0.1 K using 70 GHz phonons.

In this work we have received considerable help in the form of μ-wave equipment from Professor Stapleton of MRL and also help from Professor Anderson in MRL who is experienced in the study of Kapitza boundary resistance at low temperatures.

Publications: (01 07 74 - 30 06 75)

E. L. Griffin and J. M. Mochel
Low Temperature Thin Film NiCr Thermometers
Review of Scientific Instruments 45, 1265-1267 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

T. E. Washburn, J. E. Rutledge, and J. M. Mochel
A Domain of Two Dimensional Excitations in Superfluid Helium Films
Physical Review Letters 34, 183-186 (1975)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-37892

T. E. Washburn, J. E. Rutledge, and J. M. Mochel
Surface Excitations in Thin Helium Films
Proceedings of the Israel Physical Society Conference, Haifa, Israel, July 1974 (submitted to)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-37892

T. E. Washburn, J. E. Rutledge, and J. M. Mochel
2-D Excitations in Very Thin Helium Films
Proceedings of the International Conference on Low Temperature Physics, Finland, August 1975 (submitted to)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-37892

M.S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses: (01 07 74 - 30 06 75)

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 Baer, Research Associate
Roy K. Crawford, Assistant Professor

Junior Staff: Duane R. Aadsen, Research Assistant
Steve M. Heald, Research Assistant
Albert Macrander, Research Assistant
David H. Riehl, Research Assistant

Objectives: Study of defect structure and lattice dynamics of noble gas and other molecular crystals. Noble gas crystals are model substances for testing theoretical ideas about defect formation and mobility and about lattice dynamics, when the interatomic interactions are fairly well defined also from data on the liquid and gaseous phases. In crystalline helium such effects can be studied over a broad range of densities. Quantum effects in diffusion are prominent. Defect characteristics are probed by x-ray scattering, macroscopic observation, and by Raman scattering. Crystalline methanes offer the opportunity to study many phase transitions systematically.

Approach: The principal experimental techniques employed are x-ray diffraction and Raman scattering.

Progress: (01 07 74 - 30 06 75) 1) Work on crystalline bcc ^3He continued, to elucidate a) the volume dependence of the thermal vacancy content along the melting line and b) the nature of the excitations which appear to contribute a linear term to the heat capacity.

2) Lattice parameters of methane (CH_4) were studied over the range

2.5 to 86 K, with special attention to the upper phase transition near 20.4 K, which was proven to be first order, contrary to previous macroscopic and thermal evidence. 3) Two-phonon Raman spectra from solid argon have been studied from 14 K up to the melting curve, at different pressures up to 4 kbar. 4) Impurity-induced one-phonon Raman spectra from argon-krypton mixtures at different densities have yielded new information about phonon interactions in these anharmonic systems. 5) Apparatus to study thermal vacancy content isochorically in argon and krypton was completed.

Publications: (01 07 74 - 30 06 75)

V. M. Cheng, W. B. Daniels, and R. K. Crawford
Melting Parameters of Methane and Nitrogen from 0-10 Kilobars
Physical Review B 11, 3972 (1975)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198, and by the National Science Foundation under Grants GP-7739 and GP-18573 (University 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
Physical Review (submitted to)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

M.S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses: (01 07 74 - 30 06 75)

None

2. Electron-Lattice Coupling

Electron-Phonon Interactions in Solids

Principal Investigator: John D. Dow, Ph.D.
Associate Professor of Physics

Supporting Agency: National Science Foundation

Senior Staff: John D. Dow, Associate Professor
Donald R. Franceschetti, Research Associate

Junior Staff: Harold Hjalmarson, Research Assistant (Begin 5/21/75)
Frank Lederman, Rockefeller Foundation Fellow
Donald Miller, 0.16 Research Assistant and NSF Fellow
Donald Nicholson, Research Assistant (Begin 5/21/75)
Darryl Lyle Smith, Research Assistant (Term 8/20/74)

Objectives: To propose simple theoretical models of experimental data and to stimulate experimental tests of those models in the following areas: (i) transport theory, electron-phonon interactions in metals, and thermoelectric effects in pressurized metals (the direct conversion of heat to electricity); (ii) theory of ultratransparent solids (the materials to be used in fiber-optic communications systems and in lenses for high-powered lasers); (iii) theory of light-intensity modulation by piezoelectric acoustic domains (a hopeful candidate for optical communications applications); (iv) theory of excitation energy transfer in solids on a picosecond time scale (an area that will become increasingly important as high-powered lasers are developed, as optical damage studies progress, and as studies of efficient and novel luminescent devices move into the short-time, coherent-transfer regime); (v) theory of radiationless Auger transitions in ions, atoms, and solids (these transitions limit the efficiency of light-emitting diodes, provide the basis for several spectroscopies of surface states, and limit lifetimes of x-ray excitations); (vi) theory of x-ray excited metals (these are basic studies of many-

electron processes that lead to spectroscopic fine-structure; we anticipate that by putting these spectroscopies on a firm theoretical basis and by stimulating new experiments we shall contribute to the basic understanding of electronic structure and high-energy excitations of real metals and alloys); (vii) theory of strong electric field effects on thin non-conducting films and layered materials (we have solved a two-dimensional model of electric field ionization and breakdown); (viii) studies of ligand-binding to the heme group in myoglobin (a biomaterials problem that is a direct outgrowth of our studies of catalysis); and (ix) theory of excitons in doped semiconductors (a simplified but exactly-solvable model of the effect on optical properties of interactions with a plasma).

Approach: We have used every available theoretical technique that has appeared promising. These include numerical extended-Hückel, Hartree-Fock and potental-scattering calculations; development of analytic models; exploitation of symmetry, conservation laws, and sum rules; and formal many-body theory. Whenever possible we have established theoretical connections between various different types of experiments. In selecting problems, we seek the advice and cooperation of our colleagues working in experimental areas.

Progress: (01 07 74 - 30 06 75) (i) We have computed the pressure-dependent transport coefficients of Li, Na, and K; and, in the process, have developed rules of thumb for finding thermoelectrically efficient metals, which we hope to test on the still simple metals Cu, Ag, and Au. (ii) Our theory of intrinsic electronic absorption edges appears to have been verified; this absorption, together with Rayleigh scattering and intrinsic multiphonon absorption, establishes lower bounds for the absorption

coefficients of ultratransparent solids. (iii) The theory of light modulation by piezo-electric domains has been experimentally verified. (iv) The importance of zero-phonon lines to picosecond energy transfer in semiconductors has been established theoretically; work is continuing in this area. (v) The work on Auger transitions has established that multi-electron relaxation enhances Auger rates in light atoms frequently by an order-of-magnitude, and has demonstrated the importance of relaxed one-body contributions to the rates. (vi) Our studies of x-ray edge anomalies are entering a mature phase; the early work on K-edge anomalies has passed numerous experimental tests, a promising theory of $L_{2,3}$ edge anomalies is well under way. A theory of x-ray photoemission spectroscopy is in progress. Unfortunately, the proposed cooperative emission x-ray satellite must be weaker than we had estimated--experiments failed to find it. Efforts to correlate transport and x-ray data are under way. (vii) We have cracked the field ionization problem and merely need to turn the numerical crank; (viii) extended-Hückel calculations of potential energy surfaces for binding to the heme group of myoglobin are nearing completion; and (ix) the work developing a model of excitons in doped semiconductors is completed, except for the possible application to some of F. C. Brown's data.

Publications: (01 07 74 - 30 06 75)

M. A. Bowen
The Effects of Kinetic Anisotropy and Nonlocal Pseudopotentials on Thermoelectric Power
Lettere Al Nuovo Cimento 12, 151-154 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026

Marshall A. Bowen and John D. Dow
Transport of Electrons in Compressed Li, Na, and K: Thermoelectric Powers, Resistivities and Hall Coefficients
Physical Review (1975)
Supported by the National Science Foundation under Grant DMR-72-03026

John D. Dow
Excitons in Degenerate and Non-degenerate Semiconductors
Proceedings of the 12th International Conference of Physics Semiconductors, Stuttgart (1974), p. 957-961
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39132

John D. Dow
K-edge X-ray Spectra of Mg and Other Simple Metals: The Absence of Evidence for Orthogonality Catastrophes
Physical Review B 9, 4165-4170 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39132

J. D. Dow
X-ray Edges: Broadening Mechanisms, Selection Rules, Sum Rules, Compatibility Relationships, and Orthogonality Catastrophes
Proceedings of the Fourth International Conference on Vacuum Ultraviolet Radiation Physics 8.2, 649-661 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026

John D. Dow
X-ray Edges of Free-electron Metals: Comparison of Theory with Data
Physica Fennica 9, Suppl. 51 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39132

John D. Dow, M. Bowen, Ralph Bray, D. L. Spears, and Karl Hess
Piezo-Urbach Rule for Acoustoelectric Domains in GaAs
Physical Review B 10, 4305-4308 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39132, by GH-33344x (Purdue), and by the Advanced Research Projects Agency under Contract DAHC-0213 (Purdue)

John D. Dow and Donald R. Franceschetti
Threshold Scaling Rules for Cooperative Emission of X-rays
Physics Letters 50A, 1-2 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

John D. Dow, D. R. Franceschetti, and D. L. Smith
Inelastic Electron Scattering: Tests of Many-electron Threshold Theory
Physical Review B 11, 684-689 (1975)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39132

John D. Dow, John E. Robinson, John H. Slowik, and Bernd F. Sonntag
On the Theory of Soft-X-ray Absorption Thresholds: Amorphous Mg_xSb_{1-x} Alloys and Metallic Li, Na, Mg, and Al
Physical Review B 10, 432-447 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39132, by the Advanced Research Projects Agency under Contract HC-15-67-C-0221, and by the Army Research Office (Durham)

John D. Dow and Darryl Lyle Smith
X-ray Spectra of Metallic Alloys: Many Electron Effects
Journal of Physics F: Metal Physics 3, L170-L172 (1973)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39132

John D. Dow, Darryl L. Smith, and Bernd F. Sonntag
X-ray Spectra of Aluminum
Physical Review 10, 3092-3098 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39132, and by the Army Research Office D31-124-71-G103

John D. Dow, Lewis N. Watson, and Derek J. Fabian
On the K X-ray Emission Edge-shapes of Free-electron Metals
Journal of Physics F: 4, L76-L79 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39132

Donald R. Franceschetti and John D. Dow
Auger Rates for Soft X-ray Transitions in Ionic, Atomic, and Metallic Lithium
Journal of Physics F: 4, L151-L155 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39132

John D. Dow
Urbach's Rule
Article for Optical Properties of Highly Transparent Solids, edited by S. S. Mitra and E. Bendow (Plenum Press, 1975) (submitted to)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39132

John D. Dow and Donald R. Franceschetti
The Determination of X-ray Photoemission Lineshape Asymmetries from Threshold Exponents
Physical Review Letters (submitted to)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39132

John D. Dow and John E. Robinson
Improved Compatibility Relations Applied to X-ray Thresholds
Physical Review (submitted to)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39132

John E. Robinson and John D. Dow
Phase-shift Energy Dependence and X-ray Edge Anomalies
Physical Review (submitted to)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39132

J. D. Dow
Do Any Data Support the Present Theory of X-ray Edge Anomalies?
Comments on Solid State Physics (submitted to)
Non-MRL support

J. D. Dow
Final-state Interactions in the Optical Spectra of Solids: Elements of Exciton Theory
In Optical Properties of Solids, New Developments, edited by B. O. Seraphin (submitted to)
Non-MRL support

John D. Dow
Limitations on X-ray Threshold Fine-Structures Imposed by the Gross Structures of Emission Spectra
Journal of Physics F: Metal Physics (submitted to)
Supported by the National Science Foundation under Grant GH-39132

M.S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses: (01 07 74 - 30 06 75)

Marshall Allen Bowen (J. D. Dow, Adviser)
Topics in the Theory of Condensed Matter: Diffusion Thermoelectric Power in the Alkali Metals and Electroabsorption by Acoustoelectric Domains
January 1975
Supported by the National Science Foundation under Grant DMR-72-03026

Darryl L. Smith (J. D. Dow, Adviser)
Studies of the Theory in Solids
October 1974
Supported by the National Science Foundation under Grant DMR-72-03026 and by the Advanced Research Projects Agency under Contract HC-15-67-C-0221

Electronic Structure of Alloys and Surfaces

Principal Investigator: Colin P. Flynn, Ph.D.
Professor of Physics

Supporting Agency: National Science Foundation

Senior Staff: Colin P. Flynn, Professor
Richard Blint, Research Associate
John Erskine, Research Associate (ONR)
E. L. Pollock, IBM Postdoc Fellow and Research Associate

Junior Staff: Recap Avci, Turkish Government Fellow and Research Assistant
John E. Cunningham, Research Assistant
David K. Greenlaw, Research Assistant
R. Phillip Layton, Research Assistant (ONR)
Craig Lewis, Research Assistant

Objectives: This project combines experimental and theoretical programs directed toward an improved microscopic understanding of the bulk and surface properties of solid materials and of reaction processes.

Approach: Optical and vacuum ultraviolet absorption and magneto-optic studies, together with transport measurements, are employed to investigate local excited configurations of impurities and host atoms in solids and on clean metallic surfaces. Concurrent theoretical studies elucidate the results in terms of local configurational structures. Various theoretical methods for many-particle systems are employed in classical and quantum studies of defect kinetics in solids and on the surfaces of solids, and of the reaction kinetics of free molecules.

Progress: (01 07 74 - 30 06 75) Studies of the metal-insulator transition in rare gas alkali metal thin film alloys have revealed a classic example of a microscopic percolative conductivity transition in which electron-lattice coupling, rather than electron-electron coupling, is dominant. Optical spectra in the 5-12 eV range have revealed the 4f excitations of

metallic Gd and promise to settle current controversies concerning their location. The charge transfer excitations of halogens in simple metallic solvents have been discovered and found to conform well to our earlier predictions. The spectra bear a strong similarity to exciton lines of the analogous salts. Advanced methods of quantum chemistry are being applied to the elucidation of our observed rare gas pair spectra in metals and are expected to have relevance to hole self-trapping in solid rare gases. The novel difficulty here lies in the strong spin-orbit splitting of the outer core p-hole in heavy rare gas atoms. An apparatus to study persistent excitations of impurities on clean metal surfaces is now almost complete and ready for testing, with assistance from an ONR contract. An apparatus has been designed to study photodesorption processes associated with these surface excitations, and its construction will soon begin. With new Monte Carlo methods, we have exposed the inadequacy of anharmonic perturbation expansions for thermodynamic properties and have calculated high-temperature quantities that appear, for the first time, to compare favorably with observed properties of real crystals. The same methods have been used in a first full calculation of the vacancy free energy surface $g(p,T)$ and will shortly be applied to the vacancy migration problem to provide in addition a first detailed treatment of the diffusion isotope effect. Quantum methods used previously to treat light particle hopping have been applied to the resonance mode driven migration of irradiation-induced self-interstitials in metals. The interesting result is that the annealing dynamics must maintain an essentially classical form despite the quantum lattice degeneracy at the relevant temperatures (e.g., 4°K for Pb). In further work, in part supported by ONR,

spectroscopic studies of the hydrogen excitation spectrum in metallic hosts and on clean metal surfaces are in progress. Hydrogen charge transfer and deutron exchange reactions of the form $C^{3+}+H \rightarrow C^{2+}+p$ and $CH_3^+ + HD \rightarrow CH_2D^+ + H_2$ are in the process of detailed theoretical study. Their present importance is in the hydrogen equilibrium of intergallactic clouds, but the primary motivation is the importance of these and similar reactions for proposed studies of surface catalysis.

Publications: (01 07 74 - 30 06 75)

C. P. Flynn
Charge Transfer Complexes in Metals
Comments on Solid State Physics 6, 1-6 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

C. P. Flynn
Resonance Mode Hopping and the Stage I Annealing of Metals
Thin Solid Films 25, 37-43 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

J.-P. Hansen, I. R. McDonald, and E. L. Pollock
Statistical Mechanics of Dense Ionized Matter. III: Dynamical Properties of the Classical One-Component Plasma
Physical Review A 11, 1025-1039 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026 and by an IBM Postdoctoral Fellowship

E. N. Koch and C. P. Flynn
Sharp Coupling Transition of Gd in AlGa Solvents
Physical Review B 10, 4071-4078 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

D. J. Phelps, R. Avci, and C. P. Flynn
Metal-Insulator Transition in Metal-Rare Gas Alloys
Physical Review Letters 34, 23-26 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026

R. A. Tilton and C. P. Flynn
Sharp Optical Spectra of Impurities in Metals
Physical Review Letters 34, 20-23 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026

C. P. Flynn
Comments on the X-ray Edge and Recoil Problems
Physical Review (submitted to)
Supported by the National Science Foundation under Grant DMR-72-03026 and by the Office of Naval Research under Contract NOOO14-67-A-0305-0027

D. J. Phelps and C. P. Flynn
Metal-Insulator Transition in Rare Gas - Alkali Metal Thin Films
Physical Review (submitted to)
Supported by the National Science Foundation under Grant DMR-72-03026

D. J. Phelps, R. A. Tilton, and C. P. Flynn
Threshold Absorption of Rare Gas Impurities in Metals
Physical Review (submitted to)
Supported by the National Science Foundation under Grant DMR-72-03026

E. L. Pollock
Monte Carlo Method for the Direct Calculation of Anharmonic Free Energies
Journal of Physics C (submitted to)
Supported by the National Science Foundation under Grant DMR-72-03026

R. A. Tilton and C. P. Flynn
XeAr Pair Spectra in Metals and the Structure of Excitons in Wide Gap Insulators
Physical Review (submitted to)
Supported by the National Science Foundation under Grant DMR-72-03026

R. A. Tilton, D. J. Phelps, and C. P. Flynn
Sharp Pair Spectra and Excited States of Rare Gas Impurities in Metals
Physical Review (submitted to)
Supported by the National Science Foundation under Grant DMR-72-03026

M.S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses: (01 07 74 - 30 06 75)

Daniel James Phelps (C. P. Flynn, Adviser)
Optical and Electrical Studies of Alkali Metal-Rare Gas Alloys
October 1974
Supported by the National Science Foundation under Grant DMR-72-03026 and by the Advanced Research Projects Agency under Contract HC-15-67-C-0221

Richard Alonzo Tilton, II (C. P. Flynn, Adviser)
Optical Studies of Rare Gas Impurities in Alkali Metals
October 1974
Supported by the National Science Foundation under Grant DMR-72-03026 and by the Advanced Research Projects Agency under Contract HC-15-67-C-0221

Photoemission and Photoabsorption Studies with the Use of Synchrotron Radiation

Principal Investigator: Frederick C. Brown, Ph.D.
Professor of Physics

Supporting Agency: National Science Foundation

Senior Staff: Frederick C. Brown, Professor
Michael Skibowski, Visiting Associate Professor

Junior Staff: Steve Selbrede, Teaching Assistant
Ka-Chiu Woo, Research Assistant

Objectives:

(a) Photoemission from Layer Crystals - The layer crystals MoS_2, $NbSe_2$, TaS_2, and TiS_2 and others are examples of materials which possess a nearly two dimensional band structure. In this sense, they are analogous to graphite with weak bonding between layers and strong overlap of orbitals within the basal plane. They possess a wide range of properties from semiconducting to superconducting. In addition, interesting changes in phase sometimes take place, for example from metallic to insulating, upon cooling to low temperature. These are as yet imperfectly understood and may be related to changes in periodicity associated with fluctuations in charge density upon cooling.

We propose a study of the electronic structure, especially the valence bands of these materials by high resolution photoemission. In this technique, ultraviolet or x-ray radiation is incident upon a cleaved surface of the sample and one measures the intensity versus kinetic energy of electrons photoemitted into ultrahigh vacuum. This gives information about the valence and core bands as well as about secondary processes due to Auger effect, etc.

A detailed understanding of the layer dichalcoginides, their bonding and electronic properties (both surface and bulk) might be of great practical value. Some of these materials are of importance in catalysis and are being studied by many groups including some in the energy field. Our goal, however, is for improved scientific understanding of an interesting class of solids. They share some of the properties of, and as a bridge to, the more extreme one dimensional crystals of recent interest.

(b) Soft X-ray Photoabsorption - The intrinsic lifetime of a hole in the inner 2p shell of silicon is sufficiently long that the threshold corresponding to transitions from L_3 shell to the lowest unoccupied bands in the solid is very steep (~ 0.05 eV at a photon energy of 100 eV). Above this threshold a second spin-orbit split L_2 edge appears followed by conduction-band density-of-state features [F. Brown and O. Rustgi, Physical Review Letters 28, 497 (1972)] and possible extended x-ray absorption fine structure. The observed spectrum within one or two volts of threshold is strongly enhanced probably due to electron-hole Coulomb interaction [M. Altarelli and D. Dexter, Physical Review Letters 29, 1100 (1972)]. We plan to investigate the effect of screening due to charge carriers using silicon crystals containing known amounts of donor impurity. The effective dielectric constant for phosphorus doped silicon has recently been measured and our samples will bracket the range where this ε is found to increase rapidly. High resolution absorption and wavelength derivative spectra will be obtained using the new grazing incidence vacuum ultraviolet monochromator, data acquisition system and sample chamber.

We plan to study the photoabsorption cross section as a function of photon energy in a number of metals and semiconductors. For example the

K-edges of boron and of nitrogen have not been studied with high resolution in BN. The same is true of carbon in graphite where photoabsorption data can be compared with electron energy loss. These are both examples of layer crystals which can be easily cleaved to prepare thin samples.

Early data by the DESY group indicates that the $N_{VI,VII}$ or 4f threshold for platinum (70-80 eV) is quite sharp. On the other hand, the dipole selection rules and recent calculations by J. Dow suggest that the 4f in platinum should be rounded if current thinking about the many-body singularity is correct. We would like to test this using maximum possible resolution. For comparison with the pure metal, we will prepare samples of platinum-palladium alloys.

Finally, we will make thin specimens of CaF_2, BaF_2 and SrF_2 for cross section measurements.

Approach: Certain unique capabilities for the experiments described above have been assembled by R. Bachrach, S. Hagstrom, M. Skibowski and the author at the Xerox Palo Alto Research Center and Stanford Synchrotron Radiation Project. Specifically, a new ultrahigh vacuum grazing incidence monochromator has been built for the spectral range 5-500 A (25-2500 eV). This instrument will provide a collimated high intensity soft x-ray beam with fixed exit direction. Very small samples can be used in transmission measurements.

An ultrahigh vacuum chamber and pumping system has been assembled for the photoemission experiments. The kinetic energy of the emitted electrons is measured by a novel time-of-flight method which makes use of the short (10^{-10} sec) pulses of synchrotron radiation from SPEAR. High speed data acquisition equipment converts the time of electron transit

from sample to detector into a pulse amplitude which is then stored in a pulse height analyzer. In this way each electron's energy (velocity) is recorded at once with considerable improvement of data accumulation rate.

The detector is a small high speed channel-plate array which can be rotated in polar angles θ and ϕ in front of the sample. Recent experiments by H. V. Smith and coworkers have shown considerable angular anisotropy in photoemission from TaS_2 and other compounds. These results show the behavior expected assuming specular transmission (conservation of k_{11}) through a surface cleaved in 10^{-10} Torr. Some difficulty in interpretation arises when one tries to decide how much of the observed angular data is due to band structure or ligand field effects and how much is due to final state properties or blocking by atomic layers at the surface. We believe such questions can be answered by varying photon energy, a unique capability of our apparatus.

Progress: (01 07 74 - 30 06 75)

(a) Photoemission from Layer Crystals - Detailed photoemission distributions have been obtained on crystals of $TaSe_2$, TiS_2 and HfS_2 using the new time-of-flight method. An energy resolution between 0.1 and 1.0 eV has been achieved with a one degree angular resolution. Photon energies from 32 to 250 eV have been used.

Many inner shell emission lines are observed and these seem to be asymmetrically broadened in the metals. In general the core and secondary electrons do not show strong angular variation. On the other hand, electrons photoemitted from the valence band show intricate angular effects. Our results are like those of Smith et al. except they extend to high photon energy. From our observed photon energy dependence it appears that the

variation with azimuthal angle is mainly determined by initial state k-value and orbital angular momentum rather than by shadowing or secondary effects.

The program to prepare layer crystals in the laboratory at Illinois is progressing well. New samples will shortly be available.

(b) Soft X-ray Photoabsorption - The $L_{2,3}$ edge of silicon (100 eV) has been studied in doped single crystals up to 10^{20} donor impurities per cm^3. A special technique was developed (plasma etching plus ion beam milling) to form very thin (2000 A) windows in single crystals. Free carrier absorption can be seen in the most highly doped samples. No effect is observed on the detailed $L_{2,3}$ structure however. Considering the carrier screening involved this indicates a very local excitation. In fact the spin-orbit split components are not in the expected 2:1 ratio confirming strong overlap of excited electron and core hole--an unexpected result in the present case!

Extensive data were taken on the alkaline earth fluorides, CaF_2, SrF_2 and BaF_2 out to 300 eV. The spectra are rich in structure where core thresholds and excitations occur.

The platinum alloy spectra are less singular than above showing anti-resonance behavior near the f-threshold. (Early data in the literature must be in error). Our results here are again unexpected.

The K shell threshold of hexagonal boron nitride BN shows an interesting line structure which we are studying as a function of polarization orientation.

Finally, we have obtained high resolution absorption spectra on thin films of TTF-TCNQ (in cooperation with Xerox group) at the sulfur $L_{2,3}$ edge.

These spectra are similar but a little more detailed than electron energy loss results.

Publications: (01 07 74 - 30 06 75)

F. C. Brown
Ultraviolet Spectroscopy of Solids with the Use of Synchrotron Radiation
Solid State Physics 29, 1-73 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

John D. Dow, Darryl L. Smith, and Bernd F. Sonntag
X-ray Spectra of Aluminum
Physical Review B 10, 3092-3098 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39132, and by the U.S. Army Research Office (Durham) under Contract ARO-D31-124-71-G103

John H. Slowik
Core Excitons in Amorphous Magnesium Alloys
Physical Review B 10, 416-431 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

B. Sonntag and Frederick C. Brown
Soft X-ray Response of Transition Metal Layer Crystals
Physical Review B 10, 2300-2306 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026, and by the U.S. Army Research Office (Durham) under Contract ARO-D31-124-71-G103

R. Z. Bachrach, F. C. Brown and S.B.M. Hagstrom
Photoelectron Spectroscopy by Time-of-Flight Technique Using Synchrotron Radiation
Journal of Vacuum Science Technology 12, 237 (1975)
Non-MRL support

R. Z. Bachrach, S.B.M. Hagstrom and F. C. Brown
Time of Flight Angularly Resolved Photoelectron Energy Spectroscopy Using Synchrotron Radiation
Vacuum Ultraviolet Radiation Physics, edited by E. E. Koch, R. Haensel and C. Koch (Pergamon/Vieweg, 1974), p. 795
Non-MRL support

F. C. Brown, R. Z. Bachrach, S.B.M. Hagstrom, N. Lien and C. H. Pruett
An Ultrahigh Vacuum Monochromator for Synchrotron Radiation
Vacuum Ultraviolet Radiation Physics, IV International Conference, Hamburg, July 1974, edited by E. E. Koch, R. Haensel and C. Kunz (Pergamon/Vieweg, 1974), p. 785
Non-MRL support

M.S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses: (01 07 74 - 30 06 75)

John Shi Sun Wei (F. C. Brown, Adviser)
Polaron Transport in Silver Bromide
May 1974
Supported by the National Science Foundation under Grant DMR-72-03026, and by the U.S. Army Research Office (Durham) under Contract ARO-D31-124-73-G103
(Omission from last year's report)

Phase Transitions and Electrical Conductors

Principal Investigator: Myron B. Salamon, Ph.D.
Professor of Physics

Supporting Agency: National Science Foundation

Senior Staff: Myron B. Salamon, Professor
Robert A. Craven, Research Associate

Junior Staff: Roy M. Herman, Research Assistant
Frank Lederman, Rockefeller Foundation Fellow
William Miniscalco, Research Assistant
Mark J. Schaffman, Research Assistant
Ruben Vargas, Research Assistant (Non-MRL NSF grant)

Objectives: (1) Experimental investigation of second order phase transitions directed toward tests of the theoretical concepts of scaling and universality.

(2) Studies of the properties of lower-dimensional conductors. Through analysis of the physical properties, especially as it relates to electrical conduction we hope to provide clues to the chemists which may lead to the synthesis of new, and possibly technically useful, conductors, and then to assist in the characterization of these new compounds.

(3) Measurement of the properties of superionic conductors. This is part of an interdisciplinary effort to study solid-state electrolytes thoroughly and systematically. The aim is to understand the ionic transport process, its relation to the crystal structure, and the role of cation correlations. Such an understanding can guide the development of new electrolytes having properties suitable for battery applications.

(4) Study of the exciton condensation in germanium. The critical point and transport properties of this new phase of matter are investigated.

Approach: The expertise developed to study phase transitions in magnetic materials is applied to lower-dimensional conductors and solid electrolytes. We take the view that the rapid changes in internal order near a phase

transition can be used, through their effect on various properties, to gain an understanding of the basic physical processes at work. For example, we are studying the relationship between the specific heat and ionic conductivity in $RbAg_4I_5$ with the goal of relating the cation correlations (measured by the specific heat) to the activation energy for ionic transport. These measurements are supplemented by x-ray and optical measurements in the same material (with Klein and Lazarus). A similar approach is taken in the study of the organic conductors TTF-TCNQ and TTF-Tetraethyl TCNQ, with the specific heat, electrical conductivity and thermal conductivity under study near the metal insulator transition (with Bardeen, Stucky, Klein, et al.). Supplementary measurements are made using microwave techniques and magnetic susceptibility. A non-organic one-dimensional conductor, guanidine-tetracyanoplatiante is also under investigation as a second line of research in the one-dimensional problem (with Stucky, Klein, and Slichter). Similar experiments are underway on the two-dimensional transition-metal dichalcogenides (with McMillan).

The exciton phase of Ge is being studied theoretically and experimentally. The theoretical focus is on the diffusive process in which droplets of the new phase are formed as the exciton gas itself diffuses through the crystal. Using Rayleigh scattering methods, the same diffusive properties are being studied experimentally.

Progress: (01 07 74 - 30 06 75) We have demonstrated the universal behavior of a number of magnetic systems near the critical point and have recently completed the analysis of the scaling behavior of the specific heat of Gd in magnetic fields. Evidence for a cross-over between normal planar magnetism and dipolar critical behavior has been found in Ag.

Through a study of the thermal conductivity of TTF-TCNQ we have demonstrated that the electrical current is carried by normal, heat-carrying electrons, rather than by quasi-superconducting fluctuations. Preliminary data on the conductivity, susceptibility, and microwave properties of one-dimensional conductors has been obtained. We have also carried out preliminary measurements on the relationship between the specific heat and the electrical conductivity in 2H-TaS_2.

We have shown, through an analysis of the specific heat, that the 206 K phase transition in $RbAg_4I_5$ is of the order-disorder type and have taken data on the temperature dependence of the order parameter.

A model for droplet diffusion in Ge has been developed which satisfactorily explains the spatial distribution of recombination radiation. Preliminary scattering data from the droplet phase have been obtained.

Publications: (01 07 74 - 30 06 75)

M. B. Salamon, J. W. Bray, G. DePasquali, R. A. Craven, G. Stucky, and A. Schultz
Thermal Conductivity of Tetrathiofulvalinium-Tetracyanoquinodimethane (TTF-TCNQ) Near the Metal-Insulator Transition
Physical Review B 11, 619-622 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026

M. B. Salamon and F. L. Lederman
Universality and the Critical Specific Heat of β-brass
Physical Review (Comments and Addenda) B 10, 4492-4494 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-33750

D. S. Simons and M. B. Salamon
Specific Heat and Resistivity of Gadolinium Near the Curie Point in External Magnetic Fields
Physical Review B 10, 4680-4686 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

F. L. Lederman and M. B. Salamon
Critical Behavior of the Specific Heat of Dysprosium Near the Néel Temperature
Solid State Communications 15, 1373-1376 (1974)
Supported by the National Science Foundation under Grant GH-33750

M.S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses: (01 07 74 - 30 06 75)

None

Use of Very High Pressure to Investigate the Structure of Matter

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

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

Senior Staff: Harry G. Drickamer, Professor

Junior Staff: Kevin Bieg, UI Fellow
William D. Drotning, Research Assistant
Eric Hockert, UI Fellow
John W. Hook III, Teaching Assistant (Research Assistant, summer only)
Gary L. House, Research Assistant
David I. Klick, Research Assistant
Dean J. Mitchell, Research Assistant
Craig E. Tyner, NSF Fellow
Doug Wilson, NSF Fellow

Objectives: The purpose of this project is the investigation of the electronic behavior of solids, using very high pressure as a primary tool. Present experimental techniques permit optical absorption and luminescence measurements to 160 kilobars, electrical resistance studies to 500 kilobars, x-ray diffraction measurements to 400 kilobars, and Mössbauer resonance studies to 250 kilobars.

Our approach is to study the relative displacement of one set of orbitals with respect to another as pressure increases. From such studies we can evaluate the parameters describing the ground state and excited state potential wells. Under many circumstances we observe an electronic transition to a new ground state whose properties we can also evaluate.

Projects currently active include studies of optical absorption and luminescence of impurities in alkali halides, ZnS phosphors, oxygenated phosphors

and organic crystals, as well as photochromism and photochemistry in spiropyrans, anils and titanates. The object is to develop more efficient optical materials through a better understanding of electronic excitation and energy transfer in condensed systems.

Approach: Through observation of the intensity and wavelength of luminescent radiation as interatomic distances are changed by application of hundreds of kilobars of pressure the details of electronic structure are determined.

Progress: (01 07 74 - 30 06 75) (1) We have made a thorough study of optical absorption and luminescence of organic molecules (anthacene, phenanthrene, purine and pyrimidine bases and nucleosides) in the crystalline state, in polymers and in solution. By an extension of the Drickamer-Slichter treatment we have characterized these excitations in a new and useful way. (2) We have made a thorough study of high pressure photochromism and piezochromism in bianthrones and analyzed the results. (3) High pressure luminescence studies have been initiated in doped alkali halides, in ZnS phosphors, and in oxygenated phosphors. (4) We have initiated high pressure photochromic studies on anils and spiropyrans. (5) We have completed a detailed study of the effect of pressure on the electronic structure of several ferrites and orthoferrites.

Publications: (01 07 74 - 30 06 75)

H. G. Drickamer
Exploratory Research at High Pressure
Materials Under Pressure, edited by T. Hirone (Maruzen Press Co., Tokyo, 1975) pp. 1-35
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

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.
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

D. L. Fanselow and H. G. Drickamer
High Pressure Studies of the Electronic Behavior of Bianthrones
Journal of Chemical Physics 61, 4567-4574 (1974)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

N. A. Halasa, G. DePasquali, and H. G. Drickamer
High Pressure Studies of Ferrities
Physical Review B10, 154-164 (1974)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

S. H. Moon and H. G. Drickamer
The Effect of Pressure on Hydrogen Bonds in Organic Solids
Chemical Physics 61, 48-54 (1974)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

B. Y. Okamoto and H. G. Drickamer
High Pressure Studies of Solvent Effects on Anthracene Spectra
Proceedings of the National Academy of Sciences 71, 4757-4759 (1974)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

B. Y. Okamoto and H. G. Drickamer
The Evaluation of Configuration Coordinate Parameters from High Pressure Optical Data I: Phenanthrene, Anthracene and Tetracene
Journal of Chemical Physics 61, 2870-2877 (1974)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

B. Y. Okamoto and H. G. Drickamer
The Evaluation of Configuration Coordinate Parameters from High Pressure Optical Data II: Purine and Pyrimidine Bases and Nucleosides
Journal of Chemical Physics 61, 2878-2882 (1974)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

B. Y. Okamoto, W. D. Drotning, and H. G. Drickamer
The Evaluation of Configuration Coordinate Parameters from High Pressure Absorption and Luminescence Data
Proceedings of the National Academy of Sciences 71, 2671-2674 (1974)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

Gregorio Weber, Fumio Tanaka, Byron Y. Okamoto, and H. G. Drickamer
The Effect of Pressure on the Molecular Complex of Isoalloxazine and Adenine
Proceedings of the National Academy of Sciences 71, 1264-1266 (1974)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

H. G. Drickamer
The Effect of Pressure on the Electronic States of Organic Solids
Proceedings of International Conference on Organic Synthesis,
Belgium, 1974 (submitted to)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

M.S. Theses: (01 07 74 - 30 06 75)

E. N. Hockert (H. G. Drickamer, Adviser)
The Effect of Pressure on the Electronic Spectra of Some Salicylidine
Anilines
May 1975
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

G. L. House (H. G. Drickamer, Adviser)
Effects of High Pressure on the Luminescence of Zinc Sulfide Phosphors
May 1975
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

C. E. Tyner (H. G. Drickamer, Adviser)
Effects of Pressure on Oxygen Dominated Phosphors
May 1975
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

Ph.D. Theses: (01 07 74 - 30 06 75)

Dan L. Fanselow (H. G. Drickamer, Adviser)
The Effect of High Pressure on a Series of Photochromic, Thermochromic,
and Piezochromic Bianthrones
October 1974
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

B. Y. Okamoto (H. G. Drickamer, Adviser)
The Effects of High Pressure on the Electronic Structure of Some Purines,
Pyrimidines and Aromatic Hydrocarbons
October 1974
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

Spin-Lattice Relaxation

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

Supporting Agency: National Science Foundation

Senior Staff: Harvey J. Stapleton, Professor

Junior Staff: Patrick Devaney, Research Assistant
Gordon E. Fish, Research Assistant
Richard Herrick, Research Assistant
Mark North, Research Assistant

Objectives: The purpose of these experiments is to qualitatively and quantitatively understand the various mechanisms which influence the spin-lattice relaxation rate ($1/T_1$) of paramagnetic ions in solids or frozen solutions and to apply this knowledge, when possible, to related areas such as dynamic nuclear polarization or the determination of excited ionic energy levels in paramagnetic complexes. The systems under investigation are those with relatively small crystal field splittings ($\sim 100\ cm^{-1}$) such as rare earth salts and Fe^{3+} in heme-like structures. Spins in these systems generally relax rapidly and allow for the possibility of a resonant Raman (Orbach) relaxation process via real transitions to and from an excited ionic state whose energy can be measured by relaxation studies. In the past year the emphasis has been in the following areas: (1) the development of experimental techniques for measuring spin-lattice relaxation rates in frozen solutions of heme-like structures containing Fe^{3+} in order to determine the excited state energy so that the total crystal field splitting of the S=5/2 manifold can be computed; (2) the design and construction of an electron nuclear double resonance (ENDOR) spectrometer to measure ligand hyperfine interactions in order to determine the degree of covalency involved in the paramangnetic complex; (3) the growth of large

single crystals of a host lattice which provides a site of octahedral symmetry for trivalent rare earth ions; and (4) the measurement of anisotropic spin-lattice relaxation rates in cubic crystals where the EPR spectrum is isotropic. The advantage of a cubic host for the study of spin-phonon interactions is that the number of coupling parameters required to completely describe the orbit-lattice interaction is minimized regardless of the model used. Models which require five coupling parameters in cubic symmetry would require 45 if no symmetry were present. In addition the use of a cubic host allows one to study relaxation in Γ_8 quartets, which exhibit an EPR spectrum which is anisotropic with respect to the magnetic field direction.

Approach: Our measurements of spin-lattice relaxation rates involve the two techniques of pulse-saturation/recovery and cw linewidth. With the former, relaxation times as short as 50 microseconds can be measured directly by observing the transient recovery of the EPR signal after a short saturating pulse of microwaves has reduced the EPR signal to zero. With the latter technique, the linewidth of the EPR signal is monitored at low power as a function of temperature in a region where the short spin-lattice relaxation time ($\lesssim 10^{-3}$ sec) is broadening the EPR line. Studies using these techniques at 9 and 16 GHz, with controlled temperatures between 1.5 and 30 K as a function of magnetic field direction, paramagnetic ion concentration, and nuclear isotope, provide the necessary relaxation data. In addition ENDOR studies are used to reveal the extent of covalent bonding of the paramagnetic complex in order to determine the effects of such bonding on the spin-phonon coupling.

Progress: (01 07 74 - 30 06 75)

(a) Growth of Octahedrally Coordinated Trivalent Rare Earth Salts - Large single crystals of the form Cs_2NaYCl_6 containing a small percentage of Ce^{3+} or Yb^{3+} have been grown. The rare earth site is surrounded by an octahedron of Cl^- ions. The EPR spectrum of these salts indicate that the cubic symmetry still persists at liquid helium temperatures whereas the corresponding lanthanum host was found to be non-cubic at helium temperatures. Preliminary relaxation data have been obtained in these salts.

(b) Relaxation Data on Yb^{3+} in the Cubic Lattice MgO - Preliminary relaxation data have been taken on cubic sites of Yb^{3+} in MgO. Charge compensation can produce lower symmetry sites in this salt which was grown at Oak Ridge National Laboratory.

(c) ENDOR Studies - After unsuccessful attempts to observe ENDOR signals on a heme-like Fe^{3+} structure (cytochrome P_{450}), we have just recently observed self ENDOR and ligand ENDOR for Yb^{3+} in Cs_2NaYCl_6. Analysis of the initial data is in progress.

(d) Relaxation Measurements on Fe^{3+} in Cytochrome P_{450} - The S=5/2 manifold of Fe^{3+} in this complex is split into three Kramers' doublets which are characterized by two splitting parameters D and E. The lowest doublet exhibits an anisotropic g-tensor characterized by g_x, g_y, and g_z, which in turn depend only on the ratio of E to D. If in addition one knows the energy of one of the two excited doublets, then and only then, can D and E be determined separately. Our Orbach relaxation data on this system is not yet complete over our full temperature capability, but the results indicate that the first excited doublet is 14.5 ± 0.5 K above the ground state.

Publications: (01 07 74 - 30 06 75)

R. L. Marchand
Contribution of Two Phonon Processes to the Spin-Lattice Relaxation Rate of Kramers Ions
Physical Review B 9, 4613-4617 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

R. L. Marchand, G. E. Fish, and H. J. Stapleton
Spin Lattice Relaxation in Trivalent Uranium in Anhydrous Lanthanum Trichloride
Physical Review B 11, 23-26 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026

H. J. Stapleton, R. L. Marchand, and E. R. Lemar
Hyperfine Effects on Spin-Lattice Relaxation Rates of Rare Earth Salts: Theory and Experimental Data
Physical Review B 10, 2687-2696 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

M.S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses: (01 07 74 - 30 06 75)

None

Nuclear Magnetic Resonance in Solids

Principal Investigator: Charles P. Slichter, Ph.D.
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Supporting Agency: U. S. Energy Research and Development Administration

Senior Staff: Charles P. Slichter, Professor
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Thomas J. Aton, Fellow
Stephen H. Couterié, Research Assistant
David M. Follstaedt, Research Assistant (Term 11/30/74)
James P. Long, Research Assistant
Howard E. Rhodes, Research Assistant

Objectives:

A) Magnetic Atoms in Non-magnetic Metals - Since this research, involving study of the magnetization cloud near the iron group atoms present in low concentration in copper, is described extensively in the "Significant Results", we will not repeat it in detail.

We are studying two broad aspects: (a) The Kondo effect, a challenging many-body problem and (b) The general nature of the electronic structure of the magnetic atoms. The importance of the Kondo effect is that the theory is very similar to a number of other theoretical problems, such as the theory of the effect of electron-electron couplings on the optical and x-ray absorption of solids. Moreover, this is a case where many-body techniques are required, and this is in fact leading to major theoretical advances, the work of P. W. Anderson and K. Wilson on scaling methods. At the March 1974 meeting of the American Physical Society, James Boyce of our group spoke on our experiments and K. Wilson of Cornell spoke on the theory in a session of invited

papers. Our experiment is free of many of the pitfalls of other experiments, especially their sensitivity to small concentrations of clusters of magnetic atoms. Since we are using a spectroscopic technique, we can separate absorption lines from isolated magnetic atoms from those which form clusters. We have thus been able to clarify what was a highly confused experimental state.

The importance of the work on the nature of the electronic structure is that here again we are free of pitfalls of other methods, for example, of small precipitates of the magnetic materials, and that the theory of the occurrence of magnetism in these materials is based on a set of parameters which have never previously been measured. We have hopes of deducing them from our measurements.

B) Charge Density Waves in Potassium - A few years ago, Overhauser made a proposal which sparked a large controversy. He proposed that under some circumstances the most stable arrangement of electrons in a metal was not the one usually assumed (uniform in space apart from a modulation which possesses the lattice periodicity) but was rather non-uniform. The non-uniformity could be pictured as a wave of excess (or deficient) electron charge superposed on the normal uniform charge. He called the phenomena charge density waves. The controversial nature of his proposal can well be understood if one remembers that all previous theories of metals make as their starting assumption the uniformity of charge in space.

At first, Overhauser proposed that charge density waves might occur in the alkali metals, being responsible for certain anomalous

properties reported by experimenters. It now seems to be generally agreed that one has special requirements on the shape of the Fermi surface for the charge density waves to exist, requirements not met by the alkali metals, but satisfied by substances such as TaS_2 (see below) in which recently charge density waves have been seen. For his stimulus in predicting this phenomenon, Overhauser is being awarded the Buckley Prize of the American Physical Society this year.

C) 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.

D) Nuclear Resonance Studies of Transition Metal-Chalcogonide Layer Compounds - The atomic structure of materials such as TaS_2, $NbSe_2$ can be considered to be a stack of sandwiches, each sandwich consisting of a plane of transition metal atoms with a plane of chalcogonide atoms on either side.

These compounds have many interesting properties both scientifically and for possible practical applications. A variety of materials can be intercalated between the sandwich layers. Intercalation changes the superconducting transition temperature. In the section on "Significant Results", we describe Overhauser's prediction of a new kind of electronic phase for uniform solids, one in which the electronic density is not uniform, the so-called charge density waves. The transition metal chalcogonide compounds are found to exhibit them. They were, in fact, first discovered by Gossard and Ehrenfreund using nuclear magnetic resonance. The phenomenon of charge density waves is one of the most startling and novel concepts to enter solid state physics, and provides a strong motive for studying these compounds.

We have been studying TaS_2 intercalated with hydrogen by means of nuclear magnetic resonance of the protons. The general object is to learn why hydrogen causes the superconducting transition temperature

to increase. Specifically, we hope to learn where the hydrogen goes in the lattice, about the ability of hydrogen to move in the lattice. It has been found by Wilson and colleagues at Bell Labs that TaS_2 has density waves. The basic interest in this phenomena is described above for the case of potassium metal. The hydrogen atoms presumably interact with charge density waves and thus provide a tool for studying them. A broad question is whether or not the lattice instability plays an important role in the superconductivity of those compounds, as has been postulated for the A-15 compounds, the materials possessing the highest transition temperatures found to date. If it does, one hopes to gain further insight into why some superconductors have high transition temperatures.

Approach: Nuclear magnetic resonance and novel techniques of double resonance are used in conjunction with solid state physics theory.

Progress: (01 07 74 - 30 06 75)

A) Magnetic Atoms in Non-magnetic Metals - We are completing analysis of our experiment on the Kondo effect in CuFe in which we demonstrated that despite conjectures of other workers, there is no change in the shape of the magnetization cloud around the Fe atom when the sample is cooled from well above to well below the Kondo temperature.

We studied powders of CuSc and CuTi for the first time, and completed work on CuV. For these systems which are difficult metallurgically, our work will provide some of the best measurements of the magnetic properties. We now have studied the entire iron group, Sc through Ni, by NMR.

We have been able to detect the presence of small amounts of undissolved V in CuV alloys quenched from the melt. For CuSc we detect the presence of Sc atoms in two forms, one evidently isolated Sc atoms in Cu, the other a compound (probably CuSc) but no Sc metal.

Our single crystal studies have enabled us to identify the resonances of nuclei which are first neighbors of Ni in CuNi, first and second neighbors to Co in CuCo, first, second, and third to Fe in CuFe, first and second neighbors to Mn in CuMn.

We have found from the single crystals that there is a coupling of the magnetic atom to the neighboring nuclei which has many features similar to the usual dipole-dipole coupling, but is several times larger. The term pseudodipolar coupling is ordinarily used for such a coupling. Present theories do not account for the size or assymetry of the coupling, but we are pursuing one which holds promise of explaining the results.

B) Charge Density Waves in Potassium - Several years ago, we decided to use nuclear magnetic resonance to test whether or not charge density waves existed in K metal. Our analysis showed that charge density waves could show up (1) in the Knight shift (2) in static quadrupole coupling (3) in spin lattice relaxation. We have completed these experiments and find that it is highly unlikely that there is a charge density wave (either static or a time-varying one) of the magnitude assumed by Overhauser for K. We are in the process of writing up the work for publication. We plan, however, to carry out studies of charge density waves in transition metal dichalcogonedes, systems where they are now known to occur as described below. It is interesting

to note that their discovery (in $NbSe_2$ by Gossard and Ehrenfreund) was made by nuclear magnetic resonance, the method we were using for potassium.

C) A New Method for Electrical Conductivity Measurements - We have verified the method using graphite, and have carried out preliminary work on TTF-TCNQ. We are constructing a cold stage to enable us to go to the temperature region of the conductivity peak.

D) Nuclear Resonance Studies of Transition Metal-Chalcogonide Layer Compounds - Our work began a year ago on the system TaS_2:H. We have found the proton NMR, and are studying its properties as a function of temperature and hydrogen concentration. As a by-product, in order to make samples, we have found that we can load hydrogen by heating the material under a pressure of hydrogen. We are establishing the relationship between gas pressure, temperature, and hydrogen content. We are measuring resonance line shape and spin-lattice relaxation. For some concentrations we find that the NMR line consists of several components--one broad, the other narrow. This suggests that several phases are coexisting. Our colleague, Professor McMillan, has recently completed a Landau theory describing both the static and dynamic properties of the charge density waves. These should be applicable to the NMR studies.

Publications: (01 07 74 - 30 06 75)

James B. Boyce, Thomas J. Aton, and Charles P. Slichter
NMR Study of the Electron Spin Density Near Iron Group Atoms in Cu
Proceedings of Conference on Magnetism and Magnetic Materials 18, 252-256 (1974)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

James B. Boyce, Thomas Aton, Thomas Stakelon, and Charles P. Slichter
Spin Polarization Near Iron Group Atoms in Cu
Pure Applied Chemistry 40, 141 (1974)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

Charles P. Slichter
Some Scientific Contributions of Herbert S. Gutowsky
Proceedings of International Society of Magnetic Resonance 17, 274-280 (1975)
Supported by the U.S. Energy Research and Development Administration
under Contract AT(11-1)-1198

Lawrence R. Whalley and Charles P. Slichter
Electric Field Gradients in Copper-Nickel Alloys
Physical Review B9, 3793-3796 (1974)
Supported by the U.S. Energy Research and Development Administration
under Contract AT(11-1)-1198

James B. Boyce and Charles P. Slichter
Conduction-Electron Spin Density Around Fe Impurities in Cu Above and
Below the Kondo Temperature
Physical Review (submitted to)
Supported by the U.S. Energy Research and Development Administration
under Contract AT(11-1)-1198

M.S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses: (01 07 74 - 30 06 75)

David Martin Follstaedt (C. P. Slichter, Adviser)
A Nuclear Magnetic Resonance Study of Dilute Copper-Vanadium Alloys
January 1975
Supported by the U.S. Energy Research and Development Administration
under Contract AT(11-1)-1198

Thomas S. Stakelon (C. P. Slichter, Adviser)
Nuclear Magnetic Resonance in Single Crystals of the Magnetic Alloys:
CuFe, CuCo, and CuNi
October 1974
Supported by the U.S. Energy Research and Development Administration
under Contract AT(11-1)-1198

Electronic 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

Objectives: Magnetic alloys are technologically important in various applications, such as electric motors, generators, transformers, and computer memory devices. The present project aims to contribute to a better fundamental understanding of magnetism in alloys of the 3d transition metals by studying (1) the effect of local atomic environment on the moment associated with 3d metal atoms and (2) the magnetic properties and the magnetic structure of mictomagnetic ("spin glass") alloys, which were shown in recent years to be much more prominent among atomically disordered solid solutions than previously suspected.

Approach: Magnetic susceptibility and specific heat measurements are made over a large range of temperatures upon carefully prepared and characterized alloys.

Progress: (01 07 74 - 30 06 75) (a) The experimental study of the magnetic properties of Au-V alloys from 0.5% V to 20% V in the temperature range from 1.5° to about 450°K has been completed. Ordered Au_4V was found to be ferromagnetic, as described in the literature. The large difference in the magnetization at low temperatures between the field cooled and the zero-field cooled state apparently arises not from mictomagnetism, but from an extraordinarily large hysteresis, which

is probably due to the unusually large number of the types of atomic order domains, with a correspondingly high concentration of order domain boundaries.

(b) Low alternating field susceptibility measurements on Fe_3Al with Al contents higher than stoichiometric show a sharp susceptibility peak at temperatures depending on the Al content. These alloys are ferromagnetic at around room temperature up to about 30% Al. The susceptibility peak at low temperatures indicates the presence of mictomagnetism in the 30, 30.5, 31, and 32% Al alloys. The changeover from ferromagnetism to mictomagnetism with decreasing temperature in some of these alloys is a very unusual phenomenon and it is being studied intensively.

(c) A detailed study has been started of the temperature- and field-dependence of the rate of increase in magnetization with time in zero-field cooled Cu-Mn alloys, following the application of a magnetic field. Preliminary results suggest that the previously proposed equation, describing the "quasi-viscous" behavior of such mictomagnetic alloys, is probably applicable.

(d) A new instrument has been constructed for the measurement of remanence as a function of temperature and of time in mictomagnetic alloys. This instrument is currently being tested and we hope to put it in use in the near future.

Publications: (01 07 74 - 30 06 75)

D. J. Chakrabarti
Effect of Atomic Ordering on the Magnetic Properties of Pd_3Mn and of Some More Dilute Pd-Mn Alloys
International Journal of Magnetism 6, 305-311 (1974)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

B. deMayo
Magnetism in Gold-Iron Alloys Below 14 at.% Fe
Journal of Physics and Chemistry of Solids 35, 1525-1531 (1974)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

R. D. Shull and Paul A. Beck
Mictomagnetic to Ferromagnetic Transition in Cr-Fe Alloys
AIP Conference Proceedings 24, 95-96 (1975)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

S. Mishra
Clustering Effects in Cu-Ni-Fe Alloys
Physica Status Solidi (a) 27, K121-K126 (1975)
Supported by the National Science Foundation under Grant GH-37568X

S. Mishra
The Temperature Independent Susceptibility of Paramagnetic Cu-Ni Solid Solutions
Physical Status Solidi (a) 24, K153 (1974)
Supported by the National Science Foundation under Grant GH-37568X

A. Mukhopadhyay and Paul A. Beck
The Role of Magnetic Clusters in Mictomagnetic Alloys
Solid State Communications, 16, 1067-1069 (1975)
Supported by the National Science Foundation under Grant GH-37568X

A. Mukhopadhyay, R. D. Shull and Paul A. Beck
Relaxation and Magnetic Clusters in Mictomagnetic Cu-Mn Alloys
Journal of the Less Common Metals (submitted to)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198 and the National Science Foundation under Grant GH-37568X

M.S. Theses: (01 07 74 - 30 06 75)

Arvind Parthasarathi (P. A. Beck, Adviser)
Magnetism in Cesium Chloride Type Phases in the Nickel-Aluminum and Cobalt-Aluminum Systems
May 1975
Supported by the National Science Foundation under Grant GH-37568X

Ph.D. Theses: (01 07 74 - 30 06 75)

None

3. Disordered Materials

Light Scattering from Disordered Materials

Principal Investigator: Miles V. Klein, Ph.D.
Professor of Physics

Supporting Agency: Advanced Research Projects Agency

Senior Staff: Miles V. Klein, Professor
Wayne Wozniak, Research Associate

Junior Staff: Jim E. Clemans, Research Assistant (NSF)
Robert A. Field, Research Assistant (NSF)
David Gallagher, Research Assistant
John A. Holy, Research Assistant
Kanti Jain, Research Assistant (NSF)
Shui Lai, Research Assistant (NSF)

Objectives: To study vibrational and non-vibrational, non-propagating, modes of atoms, ions, or molecular units in metals, organic and inorganic salts, and glasses. In the metals and inorganic salts the modes are those associated with the vibration and diffusion of individual atoms or ions. In glasses they are associated with rotation of small molecular units. In the organic salts, such as TTF-TCNQ they are the vibrations that are most sensitive to the state of charge-transfer. More specific objectives are: (1) To study the motion of hydrogen in bcc metals such as niobium or fcc metals such as palladium. It dissolves in such metals in random solid solution in high concentrations in the appropriate temperature range, and it affects the mechanical properties, such as fracture, and electrical properties, such as existence of superconductivity. Microscopic knowledge about the static and dynamical properties of the hydrogen atoms is incomplete; for instance, the site geometries are somewhat in question, and the effect of the hydrogen atoms on the lattice dynamics and vibrational properties is not understood. Raman and other related, light scattering techniques can add much information of this type.

(2) To study the vibrational and diffusive motions in fast ion conductors such as Na-beta alumina, alpha AgI, or Ag_4RbI_5. These are solid electrolytes characterized by rapid hopping of a large number of ions among an even larger number of sites. Their potential use in storage batteries are well known. Little is known, however, about the microscopic jump processes by which the rapidly diffusing ions actually move. Our objective is to study these motions via their effect on the vibrations of the skeleton lattice of fixed ions and directly by depolarized light scattering associated with the diffusing ions themselves. (3) To study nonpropagating modes in glasses by depolarized light scattering. These modes may be responsible for the known anomalous thermal properties of essentially all glasses over a wide range of temperatures. These are thought to be related to thermally activated relaxation processes at ordinary temperatures, perhaps by small molecular units that rotate or reorient. At low temperatures such motions may occur by tunneling. (4) To relate changes in the vibrational spectra of donor and acceptor molecules in highly conducting charge-transfer complexes such as TTF-TCNQ to the processes of charge transfer. The relationships between charge transfer from the TTF donor to the TCNQ acceptor and the high conductivity are of great interest. The loss or gain of electronic charge will affect the strength and position of vibrational infrared and Raman lines.

Approach: In most cases to meet our objectives it has been necessary to develop new techniques or extend existing techniques, mostly centered on Raman scattering and other light scattering methods. (1) The experiment on hydrogen in niobium has been carried out jointly with Professor H. Birnbaum of the Department of Metallurgical Engineering. It has required

the construction of a high vacuum chamber with windows for the Raman experiment in which the Nb sample can be outgassed and then charged with hydrogen. The Raman experiments are performed in situ. (2) The Raman part of the work on fast ion conductors is straightforward. Close-in spectra due to the diffusing ions require a multiply-passed Fabry-Perot interferometer and the use of special techniques with a Raman double grating spectrometer. The key to these studies, however, is not so much instrumentation as the availability of suitable samples, which are being prepared in our laboratory. (3) The approach for the study of non-propagating modes in glasses also requires the ability to measure close-in Raman-like spectra with a grating monochromator and with a multiply-passed Fabry-Perot. A sample cell to cover a wide range of temperature from helium temperature to the glass-transition temperature is also necessary. (4) The work on TTF-TCNQ and related materials requires firstly a suitable range of samples obtained from Professor Stucky and Professor DePasquali of the Materials Research Laboratory, and then the use of infrared and Raman spectroscopy. The infrared studies have been performed in collaboration with Professor T. L. Brown of the Department of Chemistry and the MRL. They have required the use of matrix isolation techniques and films evaporated at moderate and low temperatures on salt crystal substrates. The Raman techniques have required a wide variety of laser wavelengths from argon and krypton lasers as well as some use of a cw die laser that uses rhodamine 6G as the lasing medium.

Progress: (01 07 74 - 30 06 75) Preliminary results have been obtained in a Raman scattering experiment on hydrogen in niobium. A high vacuum, high temperature Raman cell was built in which a Nb crystal could be

heated to 700°C at 10^{-7} Torr and then exposed to a hydrogen atmosphere. Before heating of an electropolished sample two peaks in the Raman spectrum were found at 1350 and 1600 cm^{-1} (168 and 198 MeV). These are roughly consistent with the rather inaccurate known neutron scattering results and have been interpreted as due to hydrogen atoms at tetrahedral interstitial sites. They vanish upon outgassing and usually do not return upon subsequent exposure to hydrogen. Instead, several weak Raman lines appear that are close in frequency to known Raman lines in bulk NbO_2. There is also a possibility that these lines are due to CO adsorbed onto Nb-oxide.

Niobium is known to form an oxide layer at 10^{-7} Torr. The oxide is itself metallic, and if it is thick enough, light will not be able to penetrate it and reach the bulk Nb(H) material. Auger spectroscopy has been performed in the Materials Research Laboratory Analytical Facility that shows that indeed such an oxide layer perhaps 100 Å thick has formed upon heating of Nb to a few hundred degrees at 10^{-7} Torr. Such studies have further shown that a much thinner oxide layer is formed at room temperature on an electro-polished surface. Analyses are currently underway to determine the hydrogen content of the electro-polished samples. If they show that hydrogen has been introduced by the electropolishing processes, we shall proceed to a study of Raman scattering off of a niobium sample that has been charged electrolytically with hydrogen. Meanwhile a low temperature Raman cell has been constructed for the planned experiments on Pd(H).

Much of our work on superionic conductors has been devoted to sample preparation. In particular, we have cooperated with Professors Lazarus and Salamon within the Materials Research Laboratory in growing single

crystals of Ag_4RbI_5. They are of good enough quality for specific heat measurements, but they are not yet large enough or of sufficiently good optical quality for light scattering measurements. We are trying to acquire a large beta-alumina crystal for light scattering and infrared studies. Meanwhile a high temperature Raman cell has been constructed to heat the samples in a protective atmosphere.

A theory of light scattering and dielectric loss due to relaxation modes has been developed. Since superionic conductors typically have more than one type of site in a unit cell, e.g., octahedral, tetrahedral, and trigonal sites in alpha-AgI, it was first necessary to generalize the existing theory of such modes. The general theory was then applied to the "Raman" active modes and the "infrared" active modes responsible for dielectric loss. (We use these terms because the group theoretic symmetries of these modes are the same as those lattice vibration modes that are Raman and infrared active.) The "equilibrium mode", which at zero wavevector would have zero relaxation eigenvalue has at finite k an eigenvalue Dk^2 in the absence of screening, where D is the diffusion coefficient. But screening by the mobile carriers is strong, and it will reduce the strength of this mode by many orders of magnitude. Thus light scattering by diffusive density fluctuations will be suppressed. Light scattering by the Raman-active relaxation modes occurs via fluctuations in the optical polarizability and it is not screened.

Other work done on the ARPA contract during the past year has included the development of a simple diffraction grating technique to reject the unwanted non-lasing fluorescence background from the output of a tunable dye laser. This has made it possible to use a cw dye laser for Raman studies on samples that have poor surfaces or that are highly absorbent.

We have made other improvements in instrumentation that will increase our ability to reject unwanted, stray laser light in a Raman scattering experiment. We have built a "third monochromator" to put in series with either of our Spex double grating monochromators. This instrument was made from an old Perkin-Elmer Model 99 prism monochromator, at a cost of a few hundred dollars, and it performs as well as the commercial Spex "third monochromator" that costs about $5500. We are currently developing techniques for masking the double monochromators for further reduction in their stray light.

During the past year work has been performed in our group on the vibrational spectroscopy of the highly conducting organic charge transfer complex TTF-TCNQ and related materials. In one series of measurements done jointly with members of T. L. Brown's group in the Chemistry Department, matrix samples were formed by freezing mixtures of evaporated TTF, TCNQ, or TTF-TCNQ and nitrogen onto a cooled alkali halide crystal. The infrared absorption spectra were then studied as a function of annealing temperature. Thin films of TTF-TCNQ were prepared by the same technique without the nitrogen matrix. When the low temperature matrix spectra of TTF-TCNQ are compared with those for uncomplexed TTF and TCNQ one sees new absorptions characteristic of the complex as well as features seen for uncomplexed TTF and TCNQ. The conclusion is that one has either nearly fully charge-transferred TTF-TCNQ or TTF° and TCNQ°, without any intermediate charge transfer species. When the matrix is heated the individual neutral molecules diffuse in the matrix and combine to form the complex.

The spectra of thin films deposited below 0°C show the presence of uncomplexed TTF and TCNQ; those formed above 0°C, or those annealed to above that temperature, show that only the complex is present. We conclude from these results that physical measurements, such as electrical conductivity, made on thin films of TTF-TCNQ grown by evaporation must be interpreted with caution. Those prepared at low temperatures definitely contain uncomplexed material, and those prepared at higher temperatures may perhaps contain some residual uncomplexed material, undetectable by infrared techniques.

Raman measurements have been made on single crystals of TTF, and molecular force-field calculations are being attempted to fit the data. Raman studies on crystals of TTF-TCNQ and on TCNQ in acetonitrile solution show evidence of a pre-resonance Raman effect. Work is currently in progress to characterize the relevant phenomena more clearly. It is possible that these measurements can be interpreted in terms of charge-transfer excitations of the complex.

Our group has been collaborating with Professor R. K. Crawford of the Department of Physics on measurements of Raman scattering from solid argon. The second order Raman spectra of the pure argon samples have been compared with defect-induced first order Raman spectra of samples doped with krypton. These measurements have been made in a high pressure, low temperature Raman cell, and the density-dependence of some of the spectral features has been determined. Studies of this type will yield important information about the linear and non-linear interatomic forces in the rare gas solids.

The work on glass has been mainly supported by the National Science Foundation on contract GH-37757 during the past year. Much of the time

on the glass project has been spent learning about the intricacies of our plane-parallel scanning Fabry-Perot interferometer. The mirror mounts supplied by the manufacturer were completely inadequate and had to be replaced. With the new mounts the inadequacies of the mirrors themselves have been revealed. Though nominally flat to $\lambda/200$, they are actually flat to half that or less. The reason for this attention to detail is that we must use special techniques to improve the "contrast" of our Fabry-Perot if we are to observe a weak continuous light scattering spectrum from the rotational "extra degrees of freedom" in the presence of much stronger static Rayleigh scattering from the frozen-in disorder in the glass. One of the best of these techniques is to multiple pass the interferometer, using different parts of the mirror surface for each pass. This places severe requirements on the planeness of the mirrors, requirements that ours do not yet meet. Another technique that we have available is the use of an iodine absorption cell to absorb the Rayleigh light.

We have obtained some high quality fused silica samples for the measurements and have been able to see readily the usual longitudinal and transverse Brillouin peaks.

Publications: (01 07 74 - 30 06 75)

K. Jain, W. T. Wozniak, and M. V. Klein
Use of a Diffraction Grating to Reject Fluorescence from a Tunable Dye Laser
Applied Optics 14, 811-812 (1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation under Grant GH-37757

Miles V. Klein
Electronic Raman Scattering
Raman Scattering in Solids, edited by Manuel Cardona (Springer-Verlag, 1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation under Grant GH-37757

Judith G. Peascoe, W. R. Fenner, and Miles V. Klein
Raman Scattering by the Hydroxyl Ion in KCl and KBr
Journal of Chemical Physics 60, 4208-4218 (1974)
Supported by the Advanced Research Projects Agency under Contracts DAHC-15-73-G10 and HC-15-67-C-0221 and by the National Science Foundation under Grants DMR-72-03026, GH-37757, GP-11173, and GP-28319

Kanti Jain and Miles V. Klein
Valley-Orbit Raman Scattering in Insulating and Metallic n-type Silicon
Physical Review Letters (submitted to)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation under Grant GH-37757

W. T. Wozniak, R. Sweany, G. DePasquali, T. Brown, and M. Klein
Vibrational Spectra of TTF-TCNQ: Evidence for TTF° and TCNQ° in Thin Films
Chemical Physics Letters (submitted to)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation under Grant DMR-72-03026

M.S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses: (01 07 74 - 30 06 75)

Jim E. Clemans (M. V. Klein, Adviser)
Low Temperature Thermal Conductivity Measurements on Solid Neon at Constant Volume
January 1975
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation under Grants DMR-72-03026 and GH-37757

Light Scattering in Solutions of Polymers, Macromolecules, Dense Gases, Liquids and Liquid Crystals

Principal Investigator: Willis H. Flygare, Ph.D.
Professor of Chemistry

Supporting Agency: Advanced Research Projects Agency

Senior Staff: Willis H. Flygare, Professor
Gregory R. Alms, Research Associate

Junior Staff: Sidney J. Bertucci, Research Assistant
Alan Burnham, Biophysical Trainee
Steven L. Hartford, Research Assistant (Until 5/20/75)
M. Meadows, Teaching Assistant
T. Raj, Biophysical Trainee

Objectives: The general objectives are to study the interactions of molecules in dense gases, liquids, liquid crystals, and solutions under a variety of controllable conditions. We are interested in the hydrodynamic properties of macromolecules and polymers in solution.

Approach: The primary approach in our study is to analyze the frequency spectrum and intensities of light scattering from the various systems described above. The spectrum of the light contains information about the dynamics of motion in the scattering systems. The intensities obtained from the integrated spectrum gives information about the static correlations in the system. We are studying both positional and orientational static and dynamic correlations.

Progress: (01 07 74 - 30 06 75) A comprehensive light scattering laboratory has been established with frequency analysis equipment from the audio to the gigahertz frequency range and apparatus for measurement of time correlation to periods of 1 microsecond.

Initial studies in the condensed phase revolved around the determination of the forces which are important in producing the liquid crystalline

phase in certain molecular systems. We have completed a careful study of the measurement of the spectrum and intensity of the depolarized light scattered from binary mixtures of the inert carbon tetrachloride with the liquid crystal producing molecules p-methyloxybenzylidene-n-butylaniline (MBBA), p-methylbenzylidene-n-butylaniline (MBA), and p-ethylbenzylidene-n-butylaniline (EBA). The structural analogs have been synthesized and the static orientational pair correlations (OPC) have been examined by light scattering. From the intensity of the depolarized Rayleigh scattered light, the OPC have been determined in the neat isotropic liquid and in solution with carbon tetrachloride as a function of concentration and temperature for the three molecules. The density dependence of the OPC of these molecules are analyzed in terms of the structure and polarity of the scattering molecules.

We find that the molecular size and shape (repulsive forces) largely determine the extent of orientational order in these liquids. The attractive intermolecular forces affect the orientational order (static OPC) by increasing the density (at a given temperature). In other words, we find that the repulsive forces (size and molecular shape) determine the structure of the liquid state and the onset of the liquid crystalline phase; the attractive forces appear to control the density (or temperature) at which the liquid crystalline phase will form.

Publications: (01 07 74 - 30 06 75)

G. R. Alms, T. D. Gierke, and W. H. Flygare
Depolarized Rayleigh Scattering in Liquids: The Density and Temperature Dependence of the Orientational Pair Correlations in Liquids Composed of Anisometric Molecules
Journal of Chemical Physics 61, 4083-4090 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

A. K. Burnham, G. R. Alms, and W. H. Flygare
The Local Electric Field: I. The Effect on Isotropic and Anisotropic Rayleigh Scattering
Journal of Chemical Physics 62, 3289-3297 (1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

W. H. Flygare, B. R. Ware, and S. L. Hartford
Electrophoretic Light Scattering
Molecular Electro-Optics, edited by C. T. O'Konski (Marcel Dekker, Inc., 1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation

T. D. Gierke and W. H. Flygare
Depolarized Raleigh Scattering in Liquids; Molecular Reorientation and Orientation Pair Correlations in a Nematic Liquid Crystal; MBBA
Journal of Chemical Physics 61, 2231-2240 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

J. C. McGurk, T. G. Schmalz, and W. H. Flygare
Fast Passage in Rotational Spectroscopy: Theory and Experiment
Journal of Chemical Physics 60, 4181-4188 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

J. R. Davidson, A. K. Burnham, B. Siegel, P. Beak, and W. H. Flygare
The Molecular Zeeman Effect and Magnetic Susceptibility Anisotropies of Oxazole and Isoxazole. A Magnetic Measure of Aromatic Character
Journal of the American Chemical Society 96, 7394-7402 (1974)
Supported by the National Science Foundation (Non-MRL)

J. P. Gollub, I. Chabay, and W. H. Flygare
Laser Heterodyne Study of Water Droplet Growth
Journal of Chemical Physics 61, 2139-2145 (1974)
Non-MRL support

S. L. Hartford and W. H. Flygare
Electrophoretic Light Scattering on Calf-Thymus DNA and Tobacco Mosaic Virus
Macromolecules 8, 80-87 (1975)
Supported by the National Science Foundation (Non-MRL)

S. L. Hartford, J. A. Lesnaw, W. H. Flygare, R. MacLeod, and M. E. Reichmann
Physical Properties of the New Jersey Serotype of Vesicular Stomatitis Virus and its Defective Particles
Proceedings of the National Academy of Science 72, 1202-1205 (1975)
Supported by the National Science Foundation (Non-MRL)

H. Mäder, J. Ekkers, W. Hoke, and W. H. Flygare
A π, τ, $\pi/2$ Type Pulse Sequence Method for the Determination of T_1 in Rotational Transitions
Journal of Chemical Physics 62, 4380-4388 (1975)
Supported by the National Science Foundation (Non-MRL)

T. Raj and W. H. Flygare
Diffusion Studies of Bovine Serum Albumin by Quasielastic Light Scattering
Biochemistry 13, 3337-3346 (1974)
Supported by the National Science Foundation (Non-MRL)

T. G. Schmalz, T. D. Gierke, P. Beak, and W. H. Flygare
Magnetic Susceptibility, Electron Delocalization and Aromaticity
Tetrahedron Letters 33, 2885-2890 (1974)
Supported by the National Science Foundation (Non-MRL)

G. R. Alms, A. K. Burnham and W. H. Flygare
Measurement of the Dispersion in Polarizability Anisotropies
Journal of Chemical Physics (submitted to)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

M.S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses: (01 07 74 - 30 06 75)

T. D. Gierke (W. H. Flygare, Adviser)
Depolarized Rayleigh Light Scattering Studies of Orientational Pair Correlations in a Nematic Liquid Crystal. The Coupled Translational-Rotational Diffusion of Rod-Like Macromolecules and the Method of Atom Dipoles
October 1974
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

S. L. Hartford (W. H. Flygare, Adviser)
Quasielastic Rayleigh Laser Light Scattering from Macromolecules, Electrophoretic Light Scattering, and the Molecular Zeeman Effect and Deuterium Coupling Constant in Methinophosphide
May 1975
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation

Dynamic Structure of Supercritical Dense Water and Aqueous Electrolyte Solutions

Principal Investigators: Jiri Jonas, Ph.D.
Professor of Chemistry

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

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

Senior Staff: Jiri Jonas, Professor
Harry G. Drickamer, Professor
John W. Linowski, Research Associate

Junior Staff: Michael Fury, Research Assistant
T. DeFries, Graduate Student (ARPA)

Objectives: The overall goal of the proposed research is the exploration of the dynamic and static structure of matter at high temperature and pressure. Nuclear magnetic resonance measurements will be made on the dynamic structure of liquids to temperatures of 1300°K and to pressures of 5 to 10 kbars. Thermoluminescence data will be obtained on a variety of materials, ultimately to 1000°K and 100 kilobars, to clarify the electronic structure of glasses, polymers, and laser materials.

The main emphasis will be on NMR studies of transport properties of electrolytes in superheated compressed steam because of the existence of a proposed process for separation of uranium isotopes using this specific medium. This process is under consideration by the Oak Ridge National Laboratory. The efficiency of the isotope separation is considerably enhanced when superheated compressed steam is used as a solvent medium.

Approach: Nuclear magnetic resonance measurements determine molecular interactions and diffusion coefficients at high pressure and temperature. Analysis of observed luminescence, also at high pressure and temperature, reveals details of electronic structure of materials.

Progress: (01 07 74 - 30 06 75) Initial stages of this new project have been finished. The high temperature, high pressure NMR equipment was designed and we expect to be in operation within several months. A related study of the effects of density on hydrogen bonding in liquid ethanol was finished in order to test the NMR equipment for accuracy in chemical shift measurements by Fourier transform technique. A thermoluminescence apparatus has been constructed and is being tested. In its present form it should operate from 77°K → 500°K and to 130 kilobars.

Publications: (01 07 74 - 30 06 75)

None

M.S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses: (01 07 74 - 30 06 75)

None

High Pressure Nuclear Magnetic Resonance and Raman Study of the Dynamic Structure of Liquids, Disordered Solids, and Polymers

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

Supporting Agency: Advanced Research Projects Agency

Senior Staff: Jiri Jonas, Professor
Nan-I Liu, Research Associate (11/21/74 - 3/20/75)

Junior Staff: John H. Campbell, Research Assistant (Until 1/5/75)
David M. Cantor, Fellow
Timothy DeFries, Research Assistant

Objectives: The goal of the research is to improve our understanding of the dynamic structure of liquids, disordered solids and polymers by studying motions and interactions at the molecular level. An important feature of all our experiments is the use of pressure as an experimental variable. In a systematic way we obtain experimental data for various liquids which will enable us to draw general conclusions about the transport properties of liquids. Our studies of disordered materials focus on the nature of the order-disorder transitions and the motional freedom in the disordered phases. The relationship between polymer chain motions and the mechanical properties of various polymers when subjected to mechanical forces represents the area of interest of our experiments on polymers.

In a general sense, progress in the understanding of the liquid state may lead to development of better engineering materials as the most important engineering materials are in the liquid state at some stage of their production or fabrication. Since there exists a distinct possibility that in the future many electronic devices will be made from various organic solids, our studies of the disordered organic materials are of interest in this respect. Our experiments on polymer systems may eventually 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 forces, and what is the molecular basis for such behavior.

Approach: The main methods we are currently using are the nuclear magnetic resonance relaxation measurements and the NMR spin-echo self-diffusion experiments. Since the NMR experiments yield the zero frequency Fourier transform of the correlation functions for the appropriate motions, we also use laser Raman spectroscopy to obtain detailed time dependence of the correlation functions from the analysis of band shapes via Fourier transform deconvolution techniques. In the last several years, we gained considerable expertise in the NMR high pressure techniques and, as far as our current instrumentation is concerned, there is no other laboratory in the USA and/or abroad with comparable performance features of the high pressure NMR experimental system. Our laboratory is unique in one additional aspect, namely, we also developed instrumentation and measure PVT data and shear viscosities of fluids under high pressures and temperatures.

Progress: (01 07 74 - 30 06 75)

(a) Molecular Liquids - The NMR spin-lattice relaxation times the self-diffusion coefficients and shear viscosities have been measured for a number of molecular liquids as a function of temperature and pressure. In our high pressure experiments we separated the effects of density and temperature on molecular motions and therefore we were able to draw several general conclusions about the systems studied. The experimental results

indicate that the angular momentum relaxation in liquids can be approximated as occurring through a sequence of uncorrelated binary collisions. Both self-diffusion and shear viscosity data were successfully interpreted in terms of the rough hard sphere model of liquid which denotes a general class of systems for which collisions occur impulsively and the translational and rotational motions are coupled. The effective hard sphere diameters and their temperature dependence for various liquids were obtained from our data. The results on self-diffusion and shear viscosities were in agreement with recent molecular dynamics calculations by Alder et al. (1970).

(b) Water and Heavy Water Under High Compression - Our study of the NMR relaxation times and self-diffusion in water and heavy water show conclusively that many "anomalous" properties of water and heavy water begin to disappear under high compression. One can conclude that due to rearrangement of the hydrogen bond network due to compression,water begins to exhibit behavior more characteristic of normal monoatomic liquids. For example, there is a strong decoupling of the rotational and translational motions at high compression and the activation energy for a variety of dynamic processes decreases with increasing density. Our results on water provide an experimental verification of the recent molecular dynamics calculations (Stillinger and Rahman, 1975).

(c) Disordered Solids and Polymers - A study of the molecular motions in the disordered crystalline phase of neopentane has been finished. Our experiments concentrated on self-diffusion in this disordered plastic phase. The data indicate that the defect responsible for the self-diffusion in a plastic organic crystal is a relaxed vacancy.

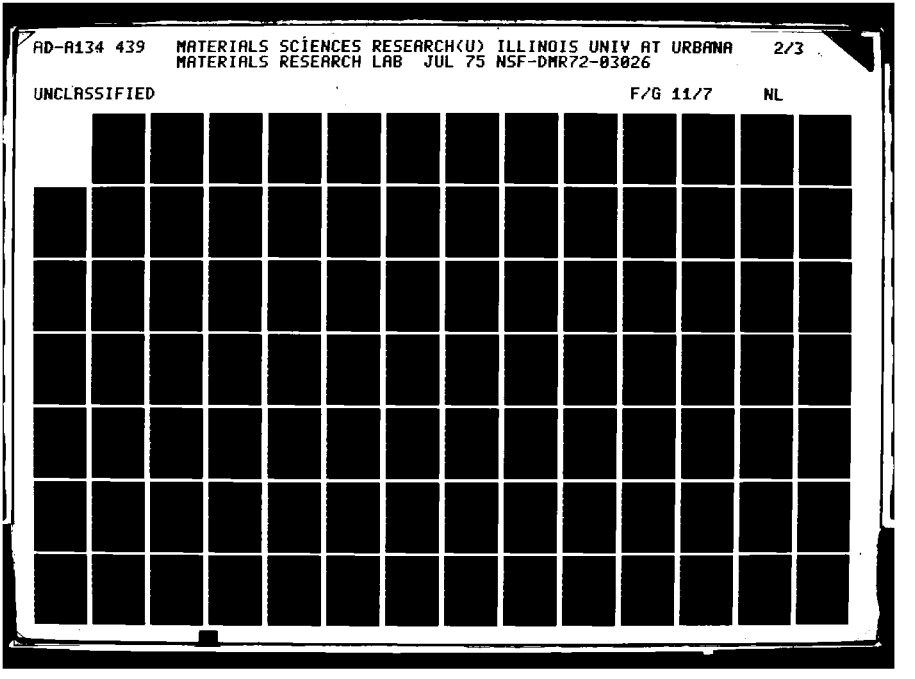
The effect of pressure on molecular motions and the glass transition temperature was measured in several elastomers, including natural rubber, synthetic cis-1,4-polyisoprene, cis-1,4-polybutadiene and natural rubber gum stock. In contrast to molecular liquids in which relaxation is dominated by volume effects the relaxation in polymeric systems has a large temperature dependence due to the temperature dependence of molecular flexibility. From the data obtained we also determined the pressure dependence of the glass transition temperature because of the close relationship between the glass transition and the segmental chain motions. It is of considerable practical interest to study the nature of this transformation in properties when a rubber polymer changes to glass, as this glass transition determined the lowest limit of the practical usefulness of the amorphous polymers.

Publications: (01 07 74 - 30 06 75)

J. Jonas
Nuclear Magnetic Resonance at High Pressure
Annual Reviews of Physical Chemistry 26, 167-190 (1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the National Science Foundation under Grant GP-28268X, and by the U.S. Air Force Office of Scientific Research under Grant AFOSR-77-2286

N.-I. Liu and J. Jonas
Pressure Effects on Molecular Motions and Glass Transition in Several Amorphous Elastomers
Journal of Magnetic Resonance 18, 465-479 (1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, and by the National Science Foundation under Grant GP-28268X

D. J. Wilbur and J. Jonas
Fourier Transform NMR in Liquids at High Pressure. III. Spin-Lattice Relaxation in Toluene-d_8
Journal of Chemical Physics 62, 2800-2807 (1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, and by the National Science Foundation under Grant GP-28268X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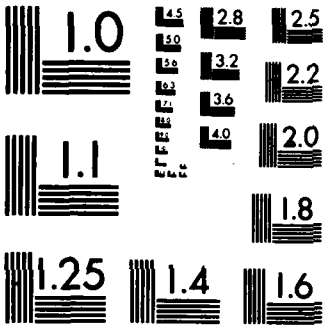


J. DeZwaan and J. Jonas
Experimental Evidence for the Rough Hard Sphere Model of Liquids by High Pressure NMR
Journal of Chemical Physics 62, 4036-4040 (1975)
Supported by the U.S. Air Force Office of Scientific Research under Grant AFOSR-77-2286

H. J. Parkhurst, Jr. and J. Jonas
Dense Liquids I. The Effect of Density and Temperature on Self-Diffusion of Tetramethylsilane and Benzene-d_6
Journal of Chemical Physics (submitted to)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, and by the National Science Foundation under Grant MPS-19428

H. J. Parkhurst, Jr. and J. Jonas
Dense Liquids II. The Effect of Density and Temperature on Viscosity of Tetramethylsilane and Benzene
Journal of Chemical Physics (submitted to)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, and by the National Science Foundation under Grant MPS-19428

M.S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses: (01 07 74 - 30 06 75)

John H. Campbell (J. Jonas, Adviser)
Raman and NMR Studies of the Effects of Density and Temperature on the Molecular Dynamics in Fluids
January 1975
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, and by the National Science Foundation under Grant GP-28268X

Hugh J. Parkhurst, Jr. (J. Jonas, Adviser)
High Pressure Nuclear Magnetic Resonance Studies of Self-Diffusion in Liquids
October 1974
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, and by the National Science Foundation under Grants DMR-72-03026 and GP-28268X

David J. Wilbur (J. Jonas, Adviser)
Fourier Transform NMR in Liquids at High Pressure
October 1974
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

Liquid Crystals and Phase Transitions

Principal Investigator: William McMillan, Ph.D.
Professor of Physics

Supporting Agency: Advanced Research Projects Agency

Senior Staff: William McMillan, Professor

Junior Staff: Ravindra Bhatt, Research Assistant
Griff L. Bilbro, Research Assistant
Kung Chao Chu, Research Assistant
Robert J. Meyer, Research Assistant
Mark P. Sears, Research Assistant

Objectives: To produce physical theories of various liquid crystal phases and to subject the theories to rigorous experimental tests. The objective, broadly speaking, is to advance liquid crystal physics from its present rather primitive state to the advanced level of solid state physics. In addition we are starting to develop the fundamental theory of charge density waves in the layered dichalcogenides (2H-$TaSe_2$).

Approach: Three theoretical approaches are being pursued vigorously: (1) Microscopic theory based on a model intermolecular interaction treated within the mean field approximation. (2) Phenomenological (Landau) theories based on the order parameter dependence of the free energy. Both static and dynamic theories are possible. (3) Wilson theory of the critical behavior near a second order phase transition. The experimental approaches being pursued at present include light scattering with a self-beating spectrometer, an optical interference technique, and adiabatic calorimetry. In the experimental work the emphasis is on precision measurements to test the theories. For charge density waves the initial approach has been to develop a Landau theory; a microscopic calculation is now under way.

Progress: (01 07 74 - 30 06 75) The technical advances this year were in three areas: experiments on liquid crystals, liquid crystal theory, and theory of charge density waves.

The experimental study has been directed toward understanding the smectic A-nematic phase transition in p-n-cyano benzylidene-octyloxy-aniline (CBOOA). We have studied both the static and dynamic properties by measuring nematic elastic constants and viscosity coefficients using a Rayleigh light scattering apparatus. Qualitatively the pretransition increase in elastic constants and viscosities predicted by theory are observed. However the phase transition is not weakly first order as predicted by one theory (Halperin, Lubensky and Ma) and the critical exponents are not helium-like as predicted by another theory (deGennes, Brochard and Janig). The experimental results are in agreement with McMillan's mean field theory. A second experiment is under way to measure the elastic properties with an order of magnitude greater precision. In this experiment the liquid crystal is distorted by an applied magnetic field and the distortion is measured by an optical interference method. I expect this work to provide the definitive experimental determination of the critical behavior of CBOOA. A precision calorimeter capable of measuring liquid crystal heat capacities to a precision of 0.2% has been constructed and tested on MBBA. We are ready to begin experiments on CBOOA.

The liquid crystal theory has progressed in several areas. Bob Meyer has constructed a successful microscopic theory two smectic phases, smectic E and smectic VI. K. C. Chu and I have constructed a unified Landau theory encompassing the nematic, smectic A and smectic C phases. The theory

predicts the static and dynamic properties of the second order nematic - smectic C phase transition and provides the impetus for an experimental study of this new area. We are currently working on the non-linear response of nematics near the nematic - smectic A phase transition. Non linear effects explain why the Freedericks transition experiment fails 0.1°C above the phase transition in CBOOA, which has been an experimental puzzle for several years. Griff Bilbro is completing a renormalization group study of the nematic - isotropic phase transition and has learned how to apply Wilson theory to weakly first order transitions.

Charge density waves (CDW) have been observed in layered transition metal dichalcogenides (1T - $TaSe_2$) and we have begun to develop the fundamental theory of CDWs. The first step was the study of a Ginzburg-Landau type theory which described the phase transitions and defects in terms of phenomenological parameters. A dynamical theory including phonon dynamics near the phase transition has been developed. Several defects in the CDW structure have been predicted theoretically. This Landau theory approach is being extended to the structural transition in A15 compounds (Nb_3Sn and V_3Si). A microscopic theory of the octahedrally coordinated layered compounds which relates CDW formation to the band structure, electron-phonon interaction, and Coulomb interaction is nearly complete. The band structure of these materials is simple enough to permit a complete, quantitative microscopic theory to be constructed. A fundamental understanding of CDWs is very important in order to understand a number of structural transitions in metals and alloys, chemical bonding in these systems and elsewhere, as well as the many one and two dimensional systems now in vogue. The layered compounds provide the ideal place to

study CDWs and to develop this fundamental theory because a variety of experiments can be done on clean, well-characterized materials.

Publications: (01 07 74 - 30 06 75)

Ravindra N. Bhatt and W. L. McMillan
Theory of Anomalous Dispersion in Liquid He^4
Physical Review A 10, 1591-1597 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

K. C. Chu and W. L. McMillan
Static and Dynamic Behavior Near a Second Order Smectic A-Nematic Phase Transition by Light Scattering
Physical Review A 11, 1059-1067 (1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

Ravindra N. Bhatt and W. L. McMillan
Theory of Phonon Dynamic Near a Charge Density Wave Instability
Physical Review (submitted to)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

K. C. Chu and W. L. McMillan
Unified Landau Theory for the Nematic, Smectic A and Smectic C Phases of Liquid Crystal
Physical Review (submitted to)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

W. L. McMillan
Landau Theory of Charge Density Waves in Transition Metal Dichalcogenides
Physical Review (submitted to)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

W. L. McMillan
Phase Transitions in Liquid Crystals
French Journal of Physics (submitted to)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

W. L. McMillan
Time Dependent Landau Theory of Charge Density Waves in Transition Metal Dichalcogenides
Physical Review (submitted to)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

W. L. McMillan
Time Dependent Unified Landau Theory for the Nematic, Smectic A and Smectic C Phases of Liquid Crystals
Physical Review (submitted to)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

R. J. Meyer
Molecular Theory of the Smectic E, H, and VI Phases
Physical Review (submitted to)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

M.S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses: (01 07 74 - 30 06 75)

None

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. Bensel, Research Associate

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

Objectives: Experimental and theoretical studies are undertaken to investigate the defect and electronic properties of classic prototype solids as a function of hydrostatic pressure and temperature to determine the basic atomic mechanisms which enter into mass, charge, and thermal transport in a wide variety of materials. Particular emphasis is placed on studies of diffusion mechanisms, thermoelectric properties, and fluctuations in electrical noise near phase transitions.

Approach: Transport phenomena are studied by radioactive tracer techniques, measurement of thermoelectric power, and observation of electrical noise. Pressure and temperature are important variables.

Progress: (01 07 74 - 30 06 75) Work has been completed on a study of co-diffusion of trace impurities in NaCl crystals and an improved theoretical model has been developed. Work is nearing completion on construction of electronic apparatus, furnaces, and cryostats to permit investigations of electrical noise in solids over a wide range of temperatures. Studies of the isotope effect for tin diffusing in titanium are nearing completion. Studies of "superionic" conductors

have been begun, with the major emphasis to date on preparation of single crystal specimens of AgI and Ag_4RbI_5.

Publications: (01 07 74 - 30 06 75)

Y. M. Cheng, P. C. Allen, and D. Lazarus
Pressure Coefficient of Thermoelectric Power of Platinum/Platinum-10% Rhodium and Chromel/alumel Thermocouples
Applied Physics Letters 26, 6-7 (1975)
Supported by the U. S. Energy and Research Development Administration under Contract AT(11-1)-1198

R. S. Hockett and David Lazarus
Search for Magneto-Flicker Noise in K
Physical Review B10, 4100-4111 (1974)
Supported by the U. S. Energy and Research Development Administration under Contract AT(11-1)-1198

Jonathon D. Weiss and D. Lazarus
Pressure Dependence of the Thermoelectric Power of Sodium Between 5°K and 14°K
Physical Review B10, 456-473 (1974)
Supported by the U.S. Energy Research and Development Administration under Contract AT(11-1)-1198

H. M. Gilder and D. Lazarus
Role of Vacancy Anharmonicity on Non-Arrhenius Diffusional Behavior
Physical Review (submitted to)
Supported by the U. S. Energy and Research Development Administration under Contract AT(11-1)-1198

Joan L. Mitchell and David Lazarus
Effect of Heterovalent Impurities Co-Diffusing with Monovalent Tracers in Ionic Crystals
Physical Review (submitted to)
Supported by the U. S. Energy and Research Development Administration under Contract AT(11-1)-1198

M.S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses: (01 07 74 - 30 06 75)

Richard Spencer Hockett (D. Lazarus, Adviser)
Search for Magneto-Flicker Noise in Potassium
October 1974
Supported by the U. S. Energy and Research Development Administration
under Contract AT(11-1)-1198

Joan Laverne Mitchell (D. Lazarus, Adviser)
Effect of Heterovalent Impurities Co-Diffusing with Monovalent Tracers in Ionic Crystals
October 1974
Supported by the U. S. Energy and Research Development Administration
under Contract AT(11-1)-1198

Radiation 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
Wolfram Hertz, Research Associate
Yan Lwin, Visiting Associate Professor (summer only)

Junior Staff: Robert C. Birtcher, Research Assistant (until 3/1/75)
Walter S. Knodle, Research Assistant
Robert Kozlowski, Graduate Student (Physics Station)
Thomas Kriisa, Research Assistant
Maria A. Menendez, Research Assistant
James E. Watson, Research Assistant (summer only)

Objectives: We wish to determine the geometrical structure, the migration and formation energies, and the physical property changes associated with the presence of defects in solids resulting from irradiation. Materials problems in reactors cannot be eliminated without such knowledge.

Approach: Length and resistivity changes due to high energy electron irradiation and subsequent annealing are used in association with theoretical studies. Defect structures are investigated by anomalous x-ray diffraction.

Progress: (01 07 74 - 30 06 75) During the past year we have: (1) Shown that Stage I annealing of lead is analogous to Stage I in copper except that the annealing occurs at much lower temperature (T_{1D}(Pb) = 4.1 K, T_{1D}(Cu) = 37 K). Gold remains anomalous. (2) Given a theory of steady state void growth in irradiated pure metals and in alloys. This paper has been accepted for publication in the Journal of Applied Physics.

We plan to electron irradiate gold at 0.5 K and hope to stop interstitial migration. We also plan to irradiate silver at 100 K

in ultra high vacuum and study the annealing near room temperature.

We believe that the anomalous results which we found previously were associated with gaseous impurities.

Publications: (01 07 74 - 30 06 75)

R. C. Birtcher, Y. Lwin, and J. S. Koehler
Isochronal Annealing of Pure Lead Irradiated at 1.5°K
Physical Review Letters 33, 899-900 (1974)
Supported by U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

J. Koehler
Decrease in the Void Growth Rate by Interstitial Trapping
Journal of Applied Physics 46, 2423-2427 (1975)
Supported by the U. S. Energy Research and Development Administratio under Contract AT(11-1)-1198

R. Berliner and J. S. Koehler
Temperature Dependence of Transmission Proton Channeling in Ag
Physical Review (submitted to)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

R. Berliner and J. S. Koehler
The Analysis of Forward Scattering Channeling Data
Radiation Effects (submitted to)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

M.S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses: (01 07 74 - 30 06 75)

Robert Charles Birtcher (J. S. Koehler, Adviser)
The Recovery of Lead After Electron Irradiation at 1.5 K
May 1975
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

4. Surfaces, Interfaces, Small Particles and Catalysis

Mass and Auger Spectroscopy of Surfaces and Thin Films

Principal Investigator: Charles A. Evans, Jr., Ph.D.
Senior Research Chemist

Supporting Agency: National Science Foundation

Senior and
Professional Staff: Charles A. Evans, Jr., Senior Research Chemist
Judith E. Baker, Research Chemist
Richard J. Blattner, Research Chemist
David S. Simons, Research Associate
Brian P. Stimpson, Research Associate (HEW)
Peter Williams, Research Chemist
Steven P. Withrow, Research Associate (3/1/75-6/30/75)

Junior Staff: Richard Linton, Graduate Student (Chemistry)
Andrew Loh, Graduate Student (Chemistry)
John R. Wallace, Graduate Student (Chemistry)

Objectives: The research in mass spectrometry and materials characterization encompasses (a) the study of basic processes involved in anal/tical spectroscopy, (b) the development of instrumentation and analytical techniques for the characterization of materials, and (c) the use of analytical techniques and instruments to study and elucidate certain problem areas and fundamental processes in materials research.

Approach: The techniques employed are primarily the microanalytical instruments available in the Materials Research Laboratory: ion microprobe mass spectrometry, scanning Auger microscopy (SAM), and scanning electron microscopy. Through the cooperative efforts with Professor J. W. Mayer and Marc-A. Nicolet of Cal Tech, we have MeV $^4He^+$ backscattering spectrometry, a variety of x-ray techniques and thin film preparation and treating facilities available to us.

Progress: (01 07 74 - 30 06 75) Significant progress has been made in several of our research efforts during FY 75.

(a) Ion Microprobe Mass Spectrometry - After much effort by Drs. D. K. Bakale and P. Williams, the ion probe attachment was put into operation as an analytical facility during FY 75. The modifications have brought the instrument up to a viable secondary ion transmission and high mass resolution capability, provided a stable, high current density negative primary ion beam capability and ~ 3 μm beam diameters. The utility of the instrument was demonstrated in two very important applications to be discussed below. Our main limitations lie in the age of the mass spectrometer and slow sample turnaround time.

(b) Mechanism of Hydrogen Embrittlement in Niobium - The ion microprobe was used to study several samples of Nb/H_2 provided by M. Grossbeck and H. K. Birnbaum of the Materials Research Laboratory and the Department of Metallurgy. The ion probe provided direct chemical analysis to substantiate their extensive indirect evidence that hydrogen embrittles niobium via stress induced precipitation of NbH followed by brittle fracture in the precipitated NbH.

(c) Toxic Element Transport in the Environment - During FY 75 we continued our cooperative study of air particulates emitted by coal-fired power plants with Professor D.F.S. Natusch of the Department of Chemistry. In a study of particulate morphology, J. E. Baker of the MRL and A. Loh of Chemistry found two very important features. Some of the air particulates were not solid by just a thin walled, hollow shell. Some of these hollow particles were empty while others contained smaller particles. The study indicates that the hollow particles containing the smaller particles lie

in the range of 20-74 μm. Our earlier studies (see thesis of J. R. Wallace) found that the smaller particles contained the highest level of toxic trace elements and it is these smaller particles which are least effectively entrained by present emission control devices. Thus the encapsulation of these smaller particles by the larger particles reduces the amount of toxic elements emitted. This natural trapping, if controllable, may provide the mechanism by which toxic element emissions may be further reduced.

The second aspect of this cooperative program has been to test our earlier hypothesis that the enhancement of toxic elements in the smaller particles results from a surface adsorption process in the power plant flue. Recent ion microprobe analyses by R. Linton and P. Williams have found surface enhancements of more than 10 different elements in two different samples of particulates. This surface layer is from 2-10 more concentrated than the underlying layers and from 25-200 Å thick.

(d) Reactions and Transport in Solid Thin Films - During FY 75 we significantly escalated our joint research efforts with Professors M-A. Nicolet and J. W. Mayer of the Cal Tech Electrical Engineering Department. This work is directed along two lines of effort: (1) The first is the study of layer structures and materials employed in semiconductor device technology. Three systems have been studied to date--annealing of PtSi in oxidizing ambients, annealing of Al on poly-Si in the 400-560°C temperature range and annealing of Au on TiW layers on single crystal Si. The most important results were from the Al/poly-Si study. The silicon was found to dissolve, transport and precipitate in the Al medium. The original bilayer structure underwent modification to the extent that the resultant

structure which contained Si crystallites in the Al layer. Poly-Si layers are commonly used as dielectrics in devices and could be shorted out by these interactions which could result from annealing steps or operation at elevated temperatures. The latter is particularly important since the kinetics of the transport would delay the dielectric failure until the device was in operation.

(2) The second area of study involved the growth of epitaxial layers by solid state transport as opposed to the present liquid and vapor phase epi techniques. The solid phase epitaxial growth (SPEG) promises to be a significantly new concept in semiconductor processing, with lower temperatures and simplified processing techniques of potential short term fall-out. Our long-range goal is to develop concepts for the economical production of photovoltaic converters using SPEG. Results during FY 75 include an understanding of the processing steps required to produce an electrically active homoepitaxial layer of Si.

(e) Other Results - We have continued our fundamental studies in secondary ionization during this year. Results include the successful testing of the quantitative correction procedure proposed by Anderson and Hinthorne and preliminary results on the production of interpretable secondary ion spectra from organic materials.

The electrohydrodynamic ionization research disclosed that the use of $SnCl_3$ as an electrolyte produced only a protonated molecular spectrum rather than the mixed protonated-cationated species found with ionic electrolytes. Careful control of the capillary geometry improve the stability of the resultant ion beam.

Publications: (01 07 74 - 30 06 75)

R. J. Blattner, J. E. Baker and C. A. Evans, Jr.
A Simple Ion Probe Attachment for Existing Mass Spectrometers
Analytical Chemistry 46, 2171-2176 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GP-33273

W. K. Chu, M-A. Nicolet, J. W. Mayer, and C. A. Evans, Jr.
Comparison of Backscattering Spectrometry and SIMS by Analysis of Ta_2O_5 Layers
Analytical Chemistry 46, 2136 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GP-33273 and by the Office of Naval Research (Cal Tech)

B. N. Colby and C. A. Evans, Jr.
Hollow-Cathode Ionization for the Mass Spectrometric Analysis of Conducting Solids
Analytical Chemistry 46, 1236-1242 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

Richard L. Davison, David F. S. Natusch, John R. Wallace, and Charles A. Evans, Jr.
Trace Metals in Fly Ash: Dependence of Concentration on Particle Size
Environmental Science and Technology 8, 1107 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GI-31605-IES-7

Charles A. Evans, Jr.
Thin Film Compositional Analysis - A Comparison of Techniques
Journal of Vacuum Science and Technology 12, 144-150 (1975)
Supported by the National Science Foundation under Grants DMR-72-03026 and GP-42330X

D. S. Simons, B. N. Colby, and C. A. Evans, Jr.
Electrohydrodynamic Ionization Mass Spectrometry - The Ionization of Liquid Glycerol and Non-Volatile Organic Solutes
Journal of Mass Spectrometry and Ion Physics 15, 291-302 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

D. K. Bakale, B. N. Colby, and C. A. Evans, Jr.
High Mass Resolution Ion Microprobe Mass Spectrometry of Complex Matrices
Analytical Chemistry (submitted to)
Supported by the National Science Foundation under Grants DMR-72-03026 and GP-33273

R. J. Blattner, C. A. Evans, Jr., S. S. Lau, J. W. Mayer, and B. M. Ullrich
Effect of Oxidizing Ambients on Platinum Silicide Formation: II Auger and Backscattering Analyses
Journal of the Electrochemical Society (submitted to)
Supported by the National Science Foundation under Grants DMR-72-03026 and MPS-74-05745, and by the Air Force Cambridge Research Laboratory (Cal Tech)

James G. Bradley, Dominique Y. Jerome, and Charles A. Evans, Jr.
A Comparison of Mass Spectra from Three Ion Probes
National Bureau of Standards Monograph on the 1974 Workshop on Ion Microprobe Mass Spectrometry (submitted to)
Supported by the National Science Foundation under Grants DMR-72-03026 and GP-42330X

Charles A. Evans, Jr.
Instrumentation for Surface and Thin Film Analysis
Analytical Chemistry (submitted to)
Supported by the National Science Foundation under Grants DMR-72-03026 and MPS-74-05745

Charles A. Evans, Jr.
Surface and Thin Film Compositional Analysis - A Description and Comparison of Techniques
Analytical Chemistry (submitted to)
Supported by the National Science Foundation under Grants DMR-72-03026 and MPS-74-05745

K. Nakamura, M-A. Nicolet, J. W. Mayer, R. J. Blattner, and C. A. Evans, Jr.
Interaction of Al Layers with Polycrystalline Si
Journal of Applied Physics (submitted to)
Supported by the National Science Foundation under Grants DMR-72-03026 and MPS-74-05745, and by the Ford Foundation and Gulf Oil Foundation (Cal Tech)

Peter Williams and C. A. Evans, Jr.
High Mass Resolution Secondary Ion Mass Spectrometry
National Bureau of Standards Monograph on the 1974 Workshop on Ion Microprobe Mass Spectrometry (submitted to)
Supported by the National Science Foundation under Grants DMR-72-03026 and GP-43220X

M.S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses: (01 07 74 - 30 06 75)

John Raymond Wallace (D.F.S. Natusch, Adviser)
The Chemical and Physical Characterization of Airborne Particulate Matter
October 1974
Supported by the National Science Foundation under Grants DMR-72-03026, GP-33273, GP-42330X, GI-31605, and by the E. I. du Pont Company

Electronic Structure of Surfaces and Solids

Principal Investigator: A. Barry Kunz, Ph.D.
Associate Professor of Physics

Supporting Agency: National Science Foundation

Senior Staff: A. Barry Kunz, Associate Professor

Junior Staff: Michael P. Guse, Research Assistant
Kent M. Hall, Research Assistant

Objectives: Previously the overriding objective of this research has been to develop ab initio techniques which permit the study of electronic structure of solids of interest in materials science. This aim of technique development is largely complete and what has previously been the secondary objective, that is the use of these techniques to study interesting physical properties of materials, has since become the primary objective of this research project. Systems of high interest in this project include: chemisorption of hydrogen and simple hydrocarbons on transition metal surfaces; energy bands in transition metal hydrides; energy bands and bonding in strong solids such as TiC; studies of surface states and excitons in non-metals.

Approach: The fundamental approach of all these studies has been similar. The initial step is solving the Hartree-Fock problem via the intermediary of the local orbitals transformation for periodic systems or by a direct application of the spin unrestricted Hartree-Fock method for cluster type problems. Secondly the effects of electron correlation and relaxation are then incorporated in the calculation (a wide variety of methods are used here to obtain high efficiency as well as theoretical cross checks). We find the inclusion of correlation and relaxation effects are of the

greatest importance. For example the occupied bands in the alkali-halides are wider than experiment by 50 - 100% and the state density at the Fermi surface of a metal is zero if correlation is ignored. The inclusion of correlation brings these items into good agreement with experiment.

Progress: (01 07 74 - 30 06 75) This year has seen us complete development of a highly accurate, efficient unrestricted Hartree-Fock code for studies of atoms, molecules or solid objects approximated by a large cluster of atoms. This technique is being successfully employed to study the chemisorption of hydrogen on surfaces of alkaline-earths and on surfaces of transition metals. These studies are aimed at obtaining a greater understanding of catalysis. This method is being extended by using mathematical approximations to some small molecular integral to allow a very large number of atoms in the cluster being studied. The practical limit in this extension seems to be about 20 transition metal atoms in the cluster. Correlation effects are included either by a multiconfiguration self-consistent field technique or by configuration interaction.

In addition to the cluster studies, we have been extending the technique of local orbitals derived band theoretic methods to studies of bands and bonds in non-insulators. Initial success has been achieved in describing the bonding of TiC.

This research project interacts strongly with that of others. The cluster techniques and studies are being performed in close collaboration with the group of Professor Flynn. The band theoretic studies of transition metal hydrides will be undertaken in close collaboration with

the experimental studies of Professor Satterthwaite. The studies of bonding in strong solids is in conjunction with the project of Professor Williams. Finally, the band theory is also used for semiconductor studies in conjunction with Professor Holonyak.

Publications: (01 07 74 - 30 06 75)

J. C. Campbell, N. Holonyak, Jr., A. B. Kunz, and M. G. Craford
Effect of Crystal Composition on "Quasi-Direct" Recombination and LED Performance in the Indirect Region of $GaAs_{1-x}P_x$:N
Applied Physics Letters 25, 44-47 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-33771, by the Advanced Research Projects Agency under Contract HC-15-73-G10, and by the Aerospace Research Lab under Contract F-33615-72-C-1506

J. C. Campbell, N. Holonyak, Jr., A. B. Kunz, and M. G. Craford
Model Calculations for Radiative Recombination in Zn-N-Doped $GaAs_{1-x}P_x$ in the Direct and Indirect Composition Region
Physical Review B 9, 4314-4322 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-33771, by the Advanced Research Projects Agency under Contract HC-15-73-G10, and by the Aerospace Research Lab under Contract F-33615-72-C-1506

J. C. Campbell, N. Holonyak, Jr., M. H. Lee, and A. B. Kunz
Recombination Processes Involving Zn and N in $GaAs_{1-x}P_x$
Physical Review B 10, 1755-1757 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-33771, by the Advanced Research Projects Agency under Contract HC-15-73-G10, and by the Aerospace Research Lab under Contract F-33615-72-C-1506

J. J. Coleman, N. Holonyak, Jr., A. B. Kunz, W. O. Groves, D. L. Keune, and M. G. Craford
Resonant Enhancement (?) of the Recombination Probability at the Nitrogen-Trap, Γ-Band Edge Crossover in $GaAs_{1-x}P_x$:N($E_N=E_\Gamma, x\equiv x_N$)
Solid State Communications 16, 319-322 (1975)
Supported by the National Science Foundation under Grants DMR-72-03026 and DMR-72-03045-A01, by the Advanced Research Projects Agency under Contract HC-15-73-G10, and by the Aerospace Research Lab under Contract F-33615-72-C-1506

J. J. Coleman, N. Holonyak, Jr., M. J. Ludowise, A. B. Kunz, M. Altarelli, W. O. Groves and D. L. Keune
Index Dispersion Above the Fundamental Band Edge in Nitrogen-Doped $GaAs_{1-y}P_y$ ($y=0.38$, $E_N>E_\Gamma$)
Physical Review Letters 33, 1566-1569 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and DMR-72-03045-A01, by the Advanced Research Projects Agency under Contract HC-15-73-G10, and by the Aerospace Research Lab under Contract F-33615-72-C-1506

T. C. Collins, A. B. Kunz and P. W. Deutsch
Calculation of Excitation Energies of Atomic Systems Using $\hat{O}\hat{A}\hat{O}$
Physical Review A 10, 1034-1040 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

T. L. Gilbert and A. B. Kunz
Single-Center Orbital Localization
Physical Review 10, 3706-3710 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

A. Barry Kunz
Calculation of Optical Absorption Edges and Photo-Emission Edges in Solids
Proceedings of the Conference on Vacuum UV Spectroscopy, Hamburg, Germany, 1974
Supported by the National Science Foundation under Grant DMR-72-03026 and
by the Aerospace Research Lab under Contract F-33615-72-C-1506

A. Barry Kunz
Distinction Between Optical Absorption Edges and Photo-Emission Edges in Solids
Journal of Physics C 7, L231-L234 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026 and
by the Aerospace Research Lab under Contract F-33615-72-C-1506

A. B. Kunz
Influence of Electron Correlation on Surface States of Nonmetallic Solids
Solid State Communications 16, 541-544 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026 and
by the Aerospace Research Lab under Contract F-33615-72-C-1506

A. Barry Kunz and Daniel J. Mickish
Electronic Structure of LiH and NaH
Physical Review B 11, 1700-1704 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026, by
the Advanced Research Projects Agency under Contract HC-04-69-C0007, and by
the Aerospace Research Lab under Contract F-33615-72-C-1506

Daniel J. Mickish, A. Barry Kunz, and T. C. Collins
Optical Properties of LiF
Physical Review B 9, 4461-4467 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

Daniel J. Mickish, A. Barry Kunz, and Sokrates T. Pantelides
Electronic Structure and Optical Properties of Metallic Calcium
Physical Review B 10, 1369-1383 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026, by
the Advanced Research Projects Agency under Contract HC-04-69-C0007, and by
the Aerospace Research Lab under Contract F-33615-72-C-1506

Sokrates T. Pantelides, Daniel J. Mickish, and A. Barry Kunz
An AB INITIO Study of the Electronic Properties of Magnesium Oxide
Solid State Communications 15, 203-205 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026, by the Advanced Research Projects Agency under Contract HC-04-69-C0007, and by the Aerospace Research Lab under Contract F-33615-72-C-1506

Sokrates T. Pantelides, Daniel J. Mickish, and A. Barry Kunz
Correlation Effects in Energy-Band Theory
Physical Review 10, 2602-2613 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39811, and by the Aerospace Research Lab under Contract F-33615-72-C-1506

S. T. Pantelides, D. J. Mickish, and A. Barry Kunz
Electronic Structure and Properties of Magnesium Oxide
Physical Review B 10, 5203-5212 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39811, and by the Aerospace Research Lab under Contract F-33615-72-C-1506

V. E. Van Doren and A. Barry Kunz
Approximate Calculation of the Electronic Structure of Solid Surfaces and Interfaces Between Material Media
Physical Review 10, 3578-3583 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026 and by the Aerospace Research Lab under Contract F-33615-72-C-1506

A. Barry Kunz
Comment on "Electron Band Structure of Solid Methane: ab initio Calculations"
Physical Review B 9, 5330-5331 (1974)
No support acknowledged

T. L. Gilbert
The Hoehenberg-Kohn Theorem for Nonlocal External Potentials
Physical Review (submitted to)
Supported by the National Science Foundation under Grant DMR-72-03026, by the U. S. Energy Research and Development Administration (Argonne), by the Advanced Research Projects Agency under Contract HC-04-69-C0007, and by the Aerospace Research Lab under Contract F-33615-72-C-1506

Michael P. Guse and A. Barry Kunz
Vacancy Relaxation and Phonon Band Calculations for Solid Argon
Physica Status Solidi (submitted to)
Supported by the National Science Foundation under Grant DMR-72-03026

M.S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses: (01 07 74 - 30 06 75)

None

Physical and Catalytic Properties of Oxides

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

Supporting Agency: National Science Foundation

Senior Staff: Gerald P. Wirtz, Associate Professor

Junior Staff: Carl L. Eggerding, Teaching Assistant
James N. Humenik, NSF Trainee
John J. Janecek, Research Assistant
David R. Kaar, NSF Fellow
Chyang J. Yu, Research Assistant

Objectives: To grow single crystals for physical properties measurements. To control defect structures in oxides to determine their effect on physical and catalytic properties. To correlate properties with crystallographic, electronic, and defect structures.

Approach: Liquid-solid and solid-solid phase equilibrium studies in rare earth-transition metal oxide systems to determine necessary conditions for crystal growth from the liquid. Annealing of Tl_2O_3 crystals in oxygen permeable cells to vary defect concentration. Characterization of solid oxides by magnetic susceptibility, thermogramimetric analysis, x-ray diffraction, optical and electron microscopy. Measurement of electrical conductivity, Hall coefficient, and Seebeck coefficient on single crystals between 4 and 300°K.

Progress: (01 07 74 - 30 06 75) X-ray diffraction, microscopic, thermogramimetric, and calorimetric data have been gathered on the La_2O_3-CoO-O_2 system in the vicinity of the $LaCoO_3$ composition. Several derivative compounds with structures related to the Perovskite structure have been identified. The data are being analyzed and compiled into a partial phase diagram over the compositional range studied.

The carrier concentration and Hall mobility of Tl_2O_3 single crystals annealed in 0.01 to 1.0 atmospheres of O_2 has been measured. Carrier concentration was decreased by annealing in higher oxygen pressures. Mobility was increased, however, compensating for the decreased carrier concentration and yielding a virtually constant conductivity over the range of O_2 pressures. Tl_2O_3 is therefore a degenerate broad band semiconductor. The high residual resistivity ($\sim 10^{-4}$ Ω - cm) is due to scattering by lattice defects. At temperatures >200°C lattice acoustical scattering is the dominant scattering process.

The catalytic reactor coupled with the residual gas analyzer continues to be used to analyze gases desorbed from ceramic powders during processing in cooperation with various ceramic engineering studies.

Publications: (01 07 74 - 30 06 75)

S. C. Sorenson, J. A. Wronkiewicz, L. B. Sis, and G. P. Wirtz
Properties of $LaCoO_3$ as a Catalyst in Engine Exhaust Gases
Bulletin of the American Ceramic Society 53, 446-449 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026 and by the Advanced Research Projects Agency under Contract SC-131

G. P. Wirtz, L. B. Sis, and J. S. Wheeler
Sublimation of MoO_3 from WO_3-MoO_3 Catalysts During the Oxidation of Toluene
Journal of Catalysis (submitted to)
Supported by the National Science Foundation under Grant DMR-72-03026

M.S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses: (01 07 74 - 30 06 75)

James N. Humenik (G. P. Wirtz and R. L. Cook, Advisers)
Reactions Between Molybdenum Disilicide and Vanadium Oxides at Elevated Temperatures
January 1975
Supported by the National Science Foundation under Grant DMR-72-03026

Vishwa Nath Shukla (G. Wirtz, Adviser)
Electronic Conduction in Thallic Oxide
October 1974
Supported by the National Science Foundation under Grant DMR-72-03026 and
by the Advanced Research Projects Agency under Contract HC-15-67-C-0221

Organometallic Compounds and Catalysis

Principal Investigator: Galen D. Stucky, Ph.D.
Professor of Inorganic Chemistry

Supporting Agency: National Science Foundation

Senior Staff: Galen D. Stucky, Professor
Giovanni DePasquali, Research Associate Professor
David Redfield, Research Associate
Arthur J. Schultz, Research Associate

Junior Staff: Gerald Delker, Research Assistant (Until 1/6/75)
Benjamin Fieselmann, Research Assistant
Rudolph Jungst, Research Assistant
Robert I. Mink, Research Assistant
Gregory Vernon, Oak Ridge National Laboratory Fellow

Objectives: The objectives of this research program are to (1) synthesize and study the electronic properties of compounds which are structurally anisotropic in one or two dimensions and which exhibit unusual electron transfer properties; (2) isolate and characterize highly reactive organometallic intermediates which are formed in polymerization and catalytic processes; (3) experimentally investigate the rearrangement which occurs in valence electron distributions in the process atoms → molecules. The long-range goals of (1) and (2) are to understand the criteria necessary for designing and synthesizing inorganic and organic materials which have respectively useful electronic and catalytic properties. The common focus of these studies is directed towards understanding the specific nature of localized and delocalized interactions at electron deficient sites which are coordinatively unsaturated.

Approach: A strong component of the program is synthetic in nature, utilizing dry box, vacuum line and low temperature techniques to prepare and chemically characterize new materials. This aspect of the program, particularly the growth of single crystals, is greatly facilitated through

collaboration with Professor G. DePasquali of the Physics Department and MRL. A variety of physical techniques are utilized in these studies including (1) low temperature neutron, x-ray and electron diffraction techniques to investigate the nature of coordination of small molecules to electron deficient metal sites as well as dynamic structural processes in single crystals of organic and inorganic "metals;" (2) heat capacity, thermal conductivity, optical spectroscopy and single crystal magnetic susceptibility measurements (with M. Salamon, C. P. Slichter, M. Klein) to characterize the electronic properties of materials of interest.

Progress: (01 07 74 - 30 06 75) Single crystal x-ray structural studies of tetrathiafulvalene (TTF) tetracyanoquinodimethane (TCNQ) at 45°, 53°, 60° and 100°K along with temperature dependent thermal conductivity and heat capacity (M. Salamon) measurements have been completed. The conclusions drawn from these studies are that

(1) there are two transitions associated with TTF TCNQ, with maxima at 53°K (heat capacity, thermal conductivity and x-ray) and at 38°K (thermal conductivity);

(2) there is no static distortion or change in symmetry associated with the first transition;

(3) the average charge transferred from TTF to TCNQ is 0.65 ± 0.15 electrons with some evidence of varying charge density with temperature.

Single crystal diffraction and magnetic susceptibility studies related to the 38°K transition are in progress. The first substituted TCNQ metallic conductor TTF 2.5 diethyl TCNQ has been structurally characterized at room temperature by x-ray crystallography. One transition at 107°K has been detected by conductivity and heat capacity

measurements (Salamon). The fact that a completely ordered metallic organic conductor can be obtained by derivitization of TCNQ is particularly important in that it demonstrates the feasibility of the chemical modification of the electronic properties of the acceptor molecule. This work is still in progress.

The catalytic coupling of organic groups and many exchange processes have been proposed to proceed via a four-centered concerted reaction intermediate. We have been able to establish the existence and detailed stereochemistry of such a species in the oxidative coupling of $C{\equiv}CC_6H_5^-$ with $(C_5H_5)_2TiCl$. The results illustrate for the first time the nature of coordination of a low valent titanium atom to an unsaturated organic molecule (in this case, 1,4 diphenyl, 1,3 butadiene) and 1,4 diphenyl, 1,3 butadiene) an essential step in the industrially important Ziegler-Natta catalysis.

Publications: (01 07 74 - 30 06 75)

D. Michael Duggan, R. G. Jungst, K. R. Mann, G. D. Stucky and D. N. Hendrickson
Electronic and Crystallograhic Study of Two Cyanide-Bridged Copper(II) Dimers. Magnetic Exchange Interactions Through a Linear Cu-CN-Cu Bridge and a Hydrogen Bonded Cu-CN...H-N-Cu System
Journal of the American Chemical Society 96, 3443-3450 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026 and by HEW PHS HL13652

R. Jungst, D. Sekutowski and G. D. Stucky
1,3 Magnetic Exchange in Linear Trimetallic Ti(III) Complexes
Journal of the American Chemical Society 96, 8108-8109 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

Rudolph Jungst and Galen Stucky
A Mono-bridged Inner Sphere Dimer. X-ray Crystal Structure of μ-cyanobis (5,7,7,12,14,14-hexamethyl 1,4,8,11-tetraazacyclotetradeca-4,11-diene) dicopper (II) perchlorate
Inorganic Chemistry 13, 2404-2408 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

Wendell E. Rhine, J. Davis and Galen Stucky
Unsaturated Organometallic Compounds of the Main Group Elements. The Isolation and Structural Properties of bis[(tetramethylethylenediamine) lithium(I)] Anthracenide
Journal of the American Chemical Society 97, 2079-2086 (1975)
Supported by the National Science Foundation under Grants DMR-72-03026 and MPS-74-23000

Wendell E. Rhine and G. D. Stucky
Unsaturated Compounds of the Main Group Elements: Indenyllithium Tetramethylethylenediamine
Journal of the American Chemical Society 97, 737-743 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026

M. B. Salamon, J. W. Bray, G. DePasquali, R. A. Craven, G. Stucky and A. Schultz
Thermal Conductivity of Tetrathiofulvalinium-Tetracyanoquinodimethane (TTF-TCNQ) Near the Metal-Insulator Transition
Physical Review B 11, 619-622 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026

D. Sekutowski, R. Jungst and G. D. Stucky
Electronic and Magnetic Properties of Linear Chain Complexes Derived from Biscyclopentadienyl Titanium(III) and of the Infinite RMX_3 Linear Chain Complexes
American Chemical Society Symposium Series 5, 142-163 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and NSF-31016X

H. Yasuda, M. Walczak, W. Rhine and G. Stucky
The Oxidation Reactions of Organolithium-N,N,N',N'-tetramethylethylene-diamine Complexes
Journal of Organometallic Chemistry 90, 123-128 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

R. Zerger, W. Rhine and G. D. Stucky
π Groups in Ion Pair Bonding. The Effect of the Cation on the Structural and Spectroscopic Properties of Fluorenyl Ion Pairs
Journal of the American Chemical Society 96, 5441-5448 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

Richard Zerger, Wendell Rhine and Galen Stucky
The Stereochemistry of Polynuclear Compounds of the Main Group Elements. The Bonding and the Effect of Metal Hydrogen Carbon Interactions in the Organolithium Compounds
Journal of the American Chemical Society 96, 6048-6055 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GP-31016

Richard Zerger and Galen Stucky
Unsaturated Organometallic Compound of the Main Group Elements. Dicyclo-pentadienylcalcium
Journal of Organometallic Chemistry 80, 7-17 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GP-31016

G. L. Delker, C. Haas, D. Seyferth and Galen D. Stucky
Molecular Structure and Bonding of a Silacyclopropane, Dimethyl-dispiro-bicyclo[4.1.0]heptane-7,2'-silacyclopropane-3'7"-bicyclo[4.1.0]heptane
Journal of the American Chemical Society (submitted to)
Supported by the National Science Foundation under Grant DMR-72-03026, and by the Massachusetts Institute of Technology, U.S. Air Force Office of Scientific Research (NC)-AFSC Grant AF-AFOSR-72-2204

Wendell E. Rhine, Galen Stucky and S. W. Peterson
A Neutron and X-ray Diffraction Investigation of Li--H--C Interactions in $LiB(CH_3)_4$
Journal of the American Chemical Society (submitted to)
Supported by the National Science Foundation under Grants DMR-72-03026 and MPS-74-23000

A. J. Schultz, Galen D. Stucky, R. H. Blessing, and P. Coppens
The Temperature Dependence of the Crystal and Molecular Structure of $\Delta^{2,2'}$ bi-1,3-dithiole [TTF] 7,7,8,8,-tetracyano-p-quinodimethane [TCNQ]
Journal of the American Chemical Society (submitted to)
Supported by the National Science Foundation under Grant DMR-72-03026 and by the State University of New York at Buffalo, N. Y.

Dennis G. Sekutowski and Galen D. Stucky
Oxidative Coupling of the Phenylethynyl Group in μ-(1-3η:2-4η-trans-trans-1,4-diphenylbutadiene)bis(bis(η-methylcyclopentadienyl)titanium)
Journal of the American Chemical Society (submitted to)
Supported by the National Science Foundation under Grants DMR-72-03026 and MPS-74-23000

Dennis G. Sekutowski and Galen D. Stucky
A Simple Oxygen Test to Use in Dry Boxes Containing a Solvent Vapor Atmosphere
Journal of Chemical Education (submitted to)
Supported by the National Science Foundation under Grants DMR-72-03026 and MPS-74-23000

Dennis G. Sekutowski and Galen D. Stucky
Synthesis and Structure of Some Biscyclopentadienyl Titanium(III) Metal Halides
Journal of Inorganic Chemistry (submitted to)
Supported by the National Science Foundation under Grants DMR-72-03026 and MPS-74-23000

Michael R. Walczak and Galen D. Stucky
The Geometry of the Stilbene Dianion in the Solid State: The Molecular Structure of Stilbene Bis(Lithium Tetramethylethylenediamine)
Journal of the American Chemical Society (submitted to)
Supported by the National Science Foundation under Grants DMR-72-03026 and GP-31016

M. W. Watson, Yu Wang, James T. Yardley and Galen Stucky
Examination of Photophysics in Cr(III) Complexes by Laser-Excited Luminescence
Journal of Inorganic Chemistry (submitted to)
Supported by the National Science Foundation under Grants DMR-72-03026 and GP-37661X

M. W. Watson, R. P. Zerger, James T. Yardley and Galen D. Stucky
Examination of Photophysics in Rare Earth Chelates by Laser-Excited Luminescence
Inorganic Chemistry (submitted to)
Supported by the National Science Foundation under Grants DMR-72-03026, MPS-74-23000 and GP-37761X

W. Wozniak, Ray L. Sweany, G. DePasquali, Miles V. Klein, and Theodore L. Brown
Vibrational Spectra of TTF-TCNQ: Evidence for TTF° and TCNQ° in Thin Films
Chemical Physical Letters (submitted to)
Supported by the National Science Foundation under Grant DMR-72-03026 and by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

Wendell Rhine and Galen D. Stucky
The Isolation of a Friedel Crafts Intermediate
Journal of Organometallic Chemistry (submitted to)
Supported by the National Science Foundation under Grant MPS-74-23000

M.S. Theses:

None

Ph.D. Theses:

Arlene McPherson (G. D. Stucky, Adviser)
Structural Studies of Low Valent Titanium Organometallic and Unsaturated Organoaluminum Compounds
January 1975
Supported by the National Science Foundation under Grant DMR-72-03026 and by the Advanced Research Projects Agency

Michael Walczak (G. D. Stucky, Adviser)
Structure, Bonding and Reactivity Studies of Unsaturated Organolithium Compounds
January 1975
Supported by the National Science Foundation under Grant DMR-72-03026 and by the Advanced Research Projects Agency

Gregory Vernon (G. D. Stucky, Adviser)
The Characterization of the 2p X-ray Photoelectron Spectra of First Row Transition Metal Element Compounds
January 1975
Supported by the Oak Ridge National Laboratory

Transition Metal Compounds and Organometallic Catalysis

Principal Investigator: Theodore L. Brown, Ph.D.
Professor of Chemistry

Supporting Agency: National Science Foundation

Senior Staff: Theodore L. Brown, Professor
Y. N. Hsieh, Research Associate
Larry W. Olson, Research Associate

Junior Staff: Jim D. Atwood, Research Assistant
Blaine H. Byers, Research Assistant (MRL) and Teaching Assistant (Department of Chemistry)
Patrick S. Ireland, Research Assistant
Raymond S. Sweany, Industrial Fellow

Objectives:

(a) Nuclear Quadrupole Resonance Spectroscopy - As described in the following section, we have been concentrating on the development of new and more powerful experimental techniques for the measurement of pure quadrupole resonance spectra. Our motivation in this endeavor has been to broaden the scope of the technique, to permit its application to a wider range of problems in chemistry. The technique is capable of providing valuable information regarding charge distributions in molecules of considerable interest in synthesis, catalysis and solid state science.

(b) Kinetics and Mechanisms of Organometallic Reactions - Our emphasis has been on the reactions of transition metal organometallic species which may be of interest in catalytic processes of technological importance. In particular, we have been concentrating on the study of transition metal hydride systems, which have been shown to be of central importance in many homogeneously and heterogeneously catalyzed reactions.

(c) Matrix Isolation Studies - We have emphasized matrix isolation studies of metal carbonyl species, and photolysis of matrix isolated carbonyl species, to obtain data on reactive carbonyl intermediates.

Approach:

(a) Nuclear Quadrupole Resonance Spectroscopy - Our efforts during this past year have been directed toward completing the development of two pulse techniques. The first of these is called adiabatic demagnetization in the lab frame, double resonance (ADLF-DR). We have completed construction of this experiment and applied it toward measurement of ^{14}N quadrupole transitions in a variety of compounds.

We have also made operational a nuclear quadrupole resonance spin echo spectrometer, with provision for double resonance. This technique has great potential for the study of low frequency quadrupole transitions such as those of ^{2}D.

(b) Kinetics and Mechanisms of Organometallic Reactions - We have made a great deal of use in our kinetics studies of ^{13}CO isotopic labelling. This has permitted us to identify the detailed character of certain reaction pathways much more rigorously than has been possible before. In addition, we have made more use than previously of photochemistry to generate reactive intermediates.

(c) Matrix Isolation Studies - In collaboration with Professor Miles Klein and Dr. Wayne Wozniak of MRL we have studied the matrix isolation and thin film IR spectra of TTF-TCNQ, TTF and TCNQ.

Progress: (01 07 74 - 30 06 75)

(a) Nuclear Quadrupole Resonance Spectroscopy - Using the ADLF-DR technique, we have observed the ^{14}N nqr spectra of a variety of nitrogen-containing systems. Most importantly, the technique has been applied successfully to the determination of ^{14}N quadrupole resonance spectra in nitrogen-containing transition metal complexes. Our work represents the first successful

effort to observe ^{14}N nqr spectra at nitrogen bound to a metal center. The technique provides valuable information regarding the bonding between nitrogen and the metal. The ADLF-DR technique is applicable to a wide range of interesting species, including those in which N_2 is coordinated to a metal. Such complexes are of great interest in connection with the mechanism of nitrogen fixation, by either naturally occurring or man-made catalytic systems.

Since the experiment has become operational, we have begun collaboration with several groups interested in obtaining the electronic structural information which the nqr technique provides. Professor John V. Rund of the Department of Chemistry, University of Arizona, is providing samples of a series of phenanthroline palladium complexes, in which we will study the ^{14}N nqr spectra due to the phenanthroline ligand, and to coordinated azide, thiocyanate, and other ligands. Professor John H. Nelson of the Department of Chemistry, University of Nevada, Reno, is providing us with several interesting samples of azide complexes of Ni, Pd, and Pt. Professor Barry Sharpless of the Department of Chemistry, Massachusetts Institute of Technology, has supplied us with an interesting osmium complex containing nitrogen in an unusual bonding situation. The nqr experiment should be very helpful in determining more about the electron distribution around nitrogen in this interesting molecule.

The spin echo double resonance (SEDOR) experiment has been applied to the determination of the ^{2}D nqr spectrum in $DMn(CO)_5$. In this molecule the deuterium and manganese spins behave essentially as isolated dipolar pairs, and it is possible using the SEDOR technique to determine

not only the quadrupole coupling constant at ^{2}D, but also the magnitude of the dipolar interaction between ^{2}D and ^{55}Mn. From the spectrum it is possible to determine the deuterium-manganese bond distance to be 1.60 Å in excellent agreement with results from a neutron diffraction study. The technique promises to be applicable to a wide range of metal-deuterium compounds, many of which are of interest in homogeneous and heterogeneous catalytic processes. We have begun a collaboration with Dr. George Parshall of Central Research, E. I. duPont & Co., to study the deuterium quadrupole coupling constant in some platinum-deuterium systems. In addition, since this nqr work fits very closely to our studies of the kinetics and mechanisms of transition metal carbonyl hydride reactions, we have undertaken a broad program of synthesis of interesting molecules for study by the SEDOR technique.

(b) Kinetics and Mechanisms of Organometallic Reactions - The most exciting results in the current year has been the discovery of a new pathway for substitution in transition metal carbonyl hydrides. We have discovered that substitution of various ligands for CO in $HRe(CO)_5$ proceeds by a radical chain process, in which as the initiating process hydrogen is abstracted from the carbonyl hydride. Very rapid substitution of this otherwise chemically inert molecule occurs via a radical chain process. Subsequent studies of this system have shown that the radical species, $Re(CO)_5$, is particularly labile, and rapidly dissociates CO. This dissociation process leaves a very reactive chemical species, $Re(CO)_4$, capable of undergoing a variety of interesting chemistry. One reaction which we have investigated is the activation of molecular hydrogen by this species. Photolysis of $Re_2(CO)_{10}$ and H_2 in hexane solution results in

the rapid formation of a variety of rhenium carbonyl hydrides. This reaction is of interest in its own right, because it leads to the formation of several molecules which are difficult to obtain by other means. In addition, however, it signifies the possibility of a more general type of chemistry which might be applicable to other molecules. In particular, it now appears quite likely that many reactions which involve metal carbonyl hydrides as intermediates, may be proceeding through radical pathways of the type which we have discovered in the rhenium system. We are actively investigating these possibilities at present.

Much of our attention has also been devoted to attempts to understand more fully the mechanisms by which certain reactions of considerable technological importance occur. In particular, we are interested in understanding more fully the mechanism by which methanol is synthesized from CO and H_2. The key to more fully understanding these reactions seems to us to lie in a better understanding of metal-hydrogen bonds, and the relationship between the strength of such bonds and the catalytic activity of metal-hydrogen systems. A major difficulty in relating the properties of homogeneous catalysts to those of heterogeneous catalysts lies in the means of comparisons. We have been attempting to find a means of bridging the gap between the wide range of surface and solid state studies which have been carried out on the one hand and the variety of spectroscopic studies of homogeneous catalytic systems on the other. Unfortunately, particularly where hydrogen is concerned, there is very little commonality in experimental techniques which provide a basis for bridging the gap. Our studies in this area are an attempt to focus on certain key experiments which might be carried out.

We have also been actively studying the mechanisms of reactions of $Co_2(CO)_8$ with various substituting ligands, and the exchange of this molecule with ^{13}CO. This particular molecule is of importance, because it forms the basis for the cobalt carbonyl catalysts which are employed in several catalytic processes. Until now, very little has been known of the kinetic behavior of $Co_2(CO)_8$. Our kinetics results show that the few reported results which are available in the literature are incorrect. There is limited evidence in our results that the substitution reactions proceed through radical intermediates. A more careful and extended experimental study will be required to more fully elucidate what is happening in these systems.

In the previous year's report, we described progress made in the study of the stereochemistry of ^{13}CO exchange in $Mn(CO)_5Br$ and $Re(CO)_5Br$. The work on these two systems has been completed and has been accepted for publication. More importantly, however, we have uncovered what appears to be a very general effect, which we have termed "cis-labilization" of ligand dissociation. The meaning of this is that the dissociative loss of CO or other groups located adjacent (cis) to a ligand X may be strongly promoted, depending on the nature of the X group. The range of kinetics behavior occasioned by the groups X is remarkably large. Our results suggest that the great variety of activity in many homogeneous catalytic systems in which dissociation of a ligand from the metal precedes the catalytically interesting step (e.g., addition of an olefin), may be due in fact to the great range of cis-labilizing influences of the various groups which may be bonded to the transition metal. Several ^{13}CO exchange and ligand substitution studies are presently underway in an effort

to more fully document and broaden the scope of our understanding of these cis-labilization effects.

(c) Matrix Isolation Studies - The studies of TTF and TCNQ and of TTF-TCNQ are reported by Professor Klein. Our studies of $Co_2(CO)_8$ are in progress, and only limited conclusions can be drawn from the work at this time.

Publications: (01 07 74 - 30 06 75)

Theodore L. Brown
Cobalt-59 Nuclear Quadrupole Resonance Spectroscopy
Accounts of Chemical Research 7, 408-415 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026, GP-6396X and GP-30256X

Blaine H. Byers and Theodore L. Brown
Activation of Molecular Hydrogen by a Transition Metal Carbonyl Radical Species
Journal of the American Chemical Society (1975)
Supported by the National Science Foundation under Grants DMR-72-03026 and MPS-71-03201

Blaine H. Byers and Theodore L. Brown
Transition Metal Carbonyl Substitution via a Radical Chain Pathway
Journal of the American Chemical Society 97, 947-948 (1975)
Supported by the National Science Foundation under Grants DMR-72-03026 and MPS-71-03201

Patrick S. Ireland, Larry W. Olson, and Theodore L. Brown
Spin Echo Double Resonance Detection of Deuterium Quadrupole Resonance Transitions in $DMn(CO)_5$
Journal of the American Chemical Society (1975)
Supported by the National Science Foundation under Grants DMR-72-03026 and MPS-71-03201

Cheryl D. Pribula, Theodore L. Brown, and Eckard Munck
Calculated and Observed Field Gradients in $[M(CO)_{5-x}P_x]^n$ Complexes
Journal of the American Chemical Society 96, 4149-4154 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026, GP-6396X and GP-30256X

Richard L. Kieft and Theodore L. Brown
^1H and ^7Li NMR Observations of Exchange Processes in Alkyllithium-ate Complexes
Journal of Organometallic Chemistry 77, 289 (1974)
Supported by the National Science Foundation under Grant MPS-71-03201

Richard L. Kieft, David P. Novak and Theodore L. Brown
Methyl Group Exchange in Methyllithium-Lithium Bromide Solutions in Diethyl Ether
Journal of Organometallic Chemistry 77, 299 (1974)
Supported by the National Science Foundation under Grant MPS-71-03201

Cheryl D. Pribula and Theodore L. Brown
Metal Ion Interactions with $Mn(CO)_5^-$ in Ether Solutions
Journal of Organometallic Chemistry 71, 415 (1974)
Supported by the National Science Foundation under Grant MPS-71-03201

Jim D. Atwood and Theodore L. Brown
Cis-Labilization of Ligand Dissociation. I. ^{13}CO Exchange and Phosphorus Ligand Substitution with $Mn(CO)_5Br$ and $Re(CO)_5Br$
Journal of the American Chemical Society (submitted to)
Supported by the National Science Foundation under Grants DMR-72-03026 and MPS-71-03201

W. T. Wozniak, R. Sweany, G. DePasquali, T. Brown, and M. Klein
Vibrational Spectra of TTF-TCNQ: Evidence for TTF° and TCNQ° in Thin Films
Chemical Physics Letters (submitted to)
Supported by the National Science Foundation under Grant DMR-72-03026 and by the Advanced Research Projects Agency under Contract HC-15-73-G10

M.S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses: (01 07 74 - 30 06 75)

Patrick S. Ireland (T. L. Brown, Adviser)
Pulse and Double Resonance Methods in Nuclear Quadrupole Resonance Spectroscopy
May 1975
Supported by the National Science Foundation under Grant DMR-72-03026

Solid State and Surface Reactions of Organic Crystals

Principal Investigator: David Y. Curtin, Ph.D.
Professor of Chemistry

Supporting Agency: National Science Foundation

Senior Staff: David Y. Curtin, Professor
Chung-Tang Lin, Research Associate

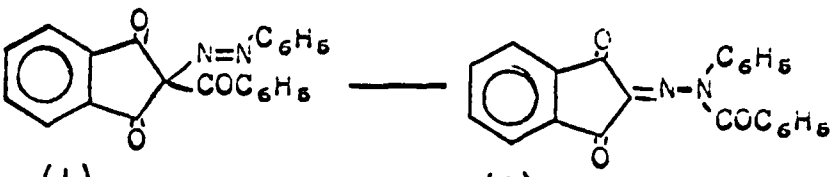
Junior Staff: Gautam Desiraju, Teaching Assistant
T. Lewis, Research Assistant (Begin 1/22/75)
Sherrill A. Puckett, Research Assistant (Until 1/22/75)

Objectives: We are interested in utilizing the unique aspects of the organic crystalline state to influence thermal reactions and reactions with gases of organic compounds. The work could have considerable practical use ultimately in the chemical industry. For example, the possibility of carrying out large-scale commercial reactions has been recognized as providing substantial savings of solvents which have been in short supply when petroleum has been scarce. The pharmaceutical, pigment, and explosives industries have long had major problems in dealing with stability of crystalline organic compounds in the appropriate crystalline form.

Approach: Our approach has been to attempt to find chemical systems with a combination of general interest and simplicity sufficient to allow fundamental knowledge to be obtained. In particular we have combined traditional organic chemical methods for studying organic reactions with microscopy, optical goniometry, x-ray crystallography (in collaboration with Dr. Iain Paul), differential scanning calorimetry, and other solid state techniques.

Progress: (01 07 74 - 30 06 75) The thermal rearrangements of 2-benzoyl-2-phenylazo-1,3-indanedione and related compounds have been investigated. Crystal structure determinations of two rearrangement products, indanetrione

sym-benzoylphenyl hydrazone (2) and its p-bromo derivative have provided conformational information bearing on the rearrangements studied.



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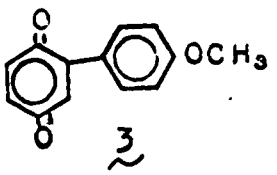
Of particular interest are solid state changes which are initiated at a limited number of nucleation sites, that is, cases in which whether or not reaction of an entire single crystal occurs is determined by whether or not an appropriate nucleation site is present (as in the reduction of silver halides in photography) [see S. R. Byrn, D. Y. Curtin, and I. C. Paul, J. Amer. Chem. Soc., 94, 890 (1972)]. We have now investigated the rearrangement of single crystals of the yellow form of the quinone 3 to the red crystalline modification and found that



3

the change begins at one (or more) sites in the crystal and the reaction front then spreads in an orderly way throughout the crystal. The crystal structure of the red (stable) form of 3 has been determined (in

collaboration with Dr. I. C. Paul) and we hope to determine the crystal structure of the yellow (metastabile) form and correlate the way in which the reaction front migrates with the crystal structure. Most important, we hope to learn more about the factors controlling the initiation of the reaction.

A study of the competition of optically active-α-phenylethylamine vapor for single crystals of a number of paired (+) and (-) optically active organic acids has shown that such crystals can be classified as (+) or (-) by visual observation of the competition. For example (+)-phenylethylamine (4) reacts preferentially with (+) single crystals of mandelic acid (5).

$C_6H_5CHNH_2CH_3$ $\quad$ $C_6H_5CHOHCOOH$

4 $\quad$ 5

The loss of acetone from the crystalline 1:1 indanetrione sym-(N-p-t-butylbenzoylphenylhydrazone acetone solvate has been studied and interpreted in terms of the x-ray crystal structure of the solvent. Both the mechanism of loss of acetone and the structure of the "crystal" remaining after the solvent has been lost are of potential future chemical interest.

Publications: (01 07 74 - 30 06 75)

David A. Dieterich, Iain C. Paul, and David Y. Curtin
Structural Studies on Nitrosobenzene and 2-Nitrosobenzoic Acid. Crystal and Molecular Structures of cis-Azobenzene Dioxide and trans-2,2'-Dicarboxyazobenzene Dioxide
Journal of the American Chemical Society 96, 6372-6380 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026 and a National Science Foundation Fellowship, and by the Advanced Research Projects Agency under Contract HC-15-67-C-0221

Chung-Tang Lin, David Y. Curtin, and Iain C. Paul
Use of Solid-Gas Reactions to Distinguish Between Left- and Right-Handed Single Crystals of an Enantiomeric Pai
Journal of the American Chemical Society 96, 6199 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

Chung-Tang Lin, Iain C. Paul, and David Y. Curtin
Anisotropic Reaction with Ammonia Gas of a Crystal of a Carboxylic Acid with Linear Hydrogen-Bonded Chains. An Example of Unitropic Attack
Journal of the American Chemical Society 96, 3699-3701 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

Rodger S. Miller, David Y. Curtin, and Iain C. Paul
Reactions of Molecular Crystals with Gases I. Reactions of Solid Aromatic Carboxylic Acids and Related Compounds with Ammonia and Amines
Journal of the American Chemical Society 96, 6329-6334 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

Rodger S. Miller, Iain C. Paul, and David Y. Curtin
Reactions of of Molecular Crystals with Gases II. The X-Ray Structure of Crystalline 4-Chlorobenzoic Acid and the Anisotropy of its Reaction with Ammonia Gas
Journal of the American Chemical Society 96, 6334-6339 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

Rodger S. Miller, David Y. Curtin, and Iain C. Paul
Reactions of Molecular Crystals with Gases III. The Relationship of Anisotropy to Crystal Structure in Reactions of Carboxylic Acids and Anhydrides with Ammonia Gas
Journal of the American Chemical Society 96, 6340-6349 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

Iain C. Paul and David Y. Curtin
Reactions of Organic Crystals with Gases
Science 187, 19-26 (1975)
Supported by the National Science Foundation under Grants DMR-72-03026 and GP-34545X

Sherrill A. Puckett, Iain C. Paul, and David Y. Curtin
1,3-Benzoyl Migration of 2-Benzoyl-2-Phenylazoindane-1,3-dione. Molecular Conformations and Crystal Structures of the Rearrangement Products, Indanetrione 2-(N-Benzoyl-N-Phenylhydrazone) and Indanetrione 2-(N-p-Bromobenzoyl-N-Phenylhydrazone)
Journal of the American Chemical Society (submitted to)
Supported by the National Science Foundation under Grant DMR-72-03026

M.S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses: (01 07 74 - 30 06 75)

Sherrill Austin Puckett (D. Y. Curtin and I. C. Paul, Advisers)
Recent Studies in Solid State Organic Chemistry
January 1975
Supported by the National Science Foundation under Grant DMR-72-03026

Nucleation and Crystal Growth in Glass Systems

Principal Investigator: Clifton G. Bergeron, Ph.D.
Professor of Ceramic Engineering

Supporting Agency: National Science Foundation

Senior Staff: Clifton G. Bergeron, Professor

Junior Staff: Lester W. Herron, Research Assistant
Charles J. Leedecke, PPG Industries Fellow
Robert A. Rita, Research Assistant

Objectives: To further our understanding of the mechanism of nucleation and crystal growth in glass-forming systems. "Glass-Ceramics", or recrystallized glasses, are a class of materials which are formed into shape in the vitreous state and are subsequently heat-treated to convert the glass to the crystalline or partially crystalline state. An enhancement of the physical, chemical, and electrical properties results. Glass-Ceramics are used as substrates and as insulation in hybrid electronic circuits, as catalyst supports for automotive exhaust systems, heat exchangers, corrosion resistant materials for high temperature applications and numerous other applications. An improved understanding of the crystallization process is important to this unique class of materials.

Approach: The growth rates of crystals from undercooled glass-forming melts are determined by hot-stage cinemicrography techniques. Information of the mobility of species in the melt and on changes in the structure of the melt during cooling are obtained by measurements of viscosity, molar volume, and electrical conductivity. The effects of additions of small quantities of selected impurities and of non-stoichiometry on the growth rates and on the morphology of the growing crystals are also being

studied. The electron microprobe is being used to determine concentration gradients at the crystal-melt interface.

Progress: (01 07 74 - 30 06 75) Both the microscopic evidence and the growth kinetic data indicate that PbB_4O_7 crystals grow from their melt by a screw dislocation mechanism. The kinetic data also indicate the existence of two crystal growth regimes, one above and the other below about 100 degrees of undercooling. There is a marked change in the activation energies for viscous flow and for electrical conduction which occurs at this undercooling. The enthalpies of activation for the interface transport process in the two growth regimes more closely resemble the values for electrical conduction than for viscous flow and thereby suggest that the transport process involved is that for the Pb^{2+} ions, perhaps on the crystal surface.

Studies of the effects of impurities on the growth rate of PbB_4O_7 have shown that Sr^{2+}, which substitutes readily for Pb^{2+} in the crystal, enhances the growth rate; the effect appears attributable to a greater mobility of Sr^{2+} on the crystal surface. Concentration gradients at the crystal-melt interface, determined from electron microprobe studies, indicate that the retardation of growth by Co^{2+} additions may be due to poisoning of kink sites on the crystal surface.

Publications: (01 07 74 - 30 06 75)

R. J. Ansems and C. G. Bergeron
Devitrification in Fiberglass Compositions, Part I
Glass Industry 56, (3) 16-22 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026 and by Australian Consolidated Industries Fiberglass Ltd.

R. J. Ansems and C. G. Bergeron
Devitrification in Fiberglass Compositions, Part II
Glass Industry 56, (4) 24-26 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026 and by Australian Consolidated Industries Fiberglass Ltd.

H. S. A. Kumar and C. G. Bergeron
Structural Interpretation of the Densities of Lead Borate Melts
Journal of the American Ceramic Society 57, 537-538 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

A. J. Marlor, C. G. Bergeron, and H. S. A. Kumar
X-ray Diffraction Data and Enthalpy of Fusion of $Cs_2B_6O_{10}$
Journal of the American Ceramic Society (Note) 57, 233 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026 and by the Advanced Research Projects Agency under Contract HC-15-67-C-0221

H. S. A. Kumar and C. G. Bergeron
Crystal Growth of Lead Tetraborate from Pure and Impurity-Doped Melts
International Journal of Crystal Growth (submitted to)
Supported by the National Science Foundation under Grant DMR-72-03026

Charles J. Leedecke and Clifton G. Bergeron
The Growth of $K_2B_8O_{13}$ in its Stoichiometric Melt
International Journal of Crystal Growth (submitted to)
Supported by the National Science Foundation under Grant DMR-72-03026 and by the Pittsburgh Plate Glass Industries Fellowship

M.S. Theses: (01 07 74 - 30 06 75)

Charles John Leedecke (C. G. Bergeron, Adviser)
The Crystallization of Potassium Octaborate from its Pure Stoichiometric Melt
October 1974
Supported by the National Science Foundation under Grant DMR-72-03026 and by the Pittsburgh Plate Glass Industries Fellowship

Lester Wynn Herron (C. G. Bergeron, Adviser)
Kinetics of Soil Removal from Catalytic Ceramic Coatings
May 1975
Supported by a Grant from Ingram-Richardson, Inc.

Ph.D. Theses: (01 07 74 - 30 06 75)

Hosakere Ananda Kumar (C. G. Bergeron, Adviser)
The Effect of Impurities on the Crystal Growth of Lead Tetraborate from its Melt
October 1974
Supported by the National Science Foundation under Grant DMR-72-03026, by the Advanced Research Projects Agency under Contract HC-15-67-C-2110, by the Owens-Corning-Fibre Glass Fellowship, and by a University of Illinois Fellowship

5. Mechanical Properties of Materials

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
C. Gregory Chen, Research Associate

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

Objectives: To understand the basic diffusion mechanisms for hydrogen and its isotopes in bcc metals over a wide temperature range. Particular interest is directed towards understanding the role of trapping mechanisms in these processes. The local vibrational modes and coupling of hydrogen to the lattice are also of interest. We have been developing measurement techniques based on anelastic, magnetic relaxation and Raman methods to study these problems.

Interest in these problems arises from the ability to study tunneling effects in light interstitial diffusion in great detail and from the importance of these physical processes in applied problems such as hydrogen embrittlement, stress corrosion, hydrogen isotope containment. These have a very wide applicability in both the fast breeder and fusion reactor programs.

Approach: A large variety of techniques are used to study hydrogen motion in metals: internal friction, magnetic relaxation, Raman scattering. Precipitation is observed with the transmission electron microscope and through measurement of elastic constants. Fracture surfaces are studied

by electron and x-ray diffraction, the ion microprobe and scanning electron microscopy.

Progress: (01 07 74 - 30 06 75) The increase of the H and D diffusion activation enthalpies with O trapping has been established over a range of compositions and temperatures. The isotope effects on the diffusive reorientation of H(D) in Fe has been established and the activation enthalpies for the relaxation processes in the Fe-D system measured. The ordering of vacancies on the H interstitial sublattice in off-stochiometric NbH has been shown and a new hydride structure determined (with Professor K. Fraser). The Nb-H system has been shown to be Raman active and the Raman technique has been applied to studying the vibrational modes of H (with Professor M. Klein).

Publications: (01 07 74 - 30 06 75)

G. Matusiewicz, R. Booker, J. Keiser and H. K. Birnbaum
On Gorsky Measurements of Hydrogen Diffusion in Niobium
Scripta Metallurgy 8, 1419-1426 (1974)
Supported by the U.S. Energy Research and Development Administration under Contract AT(11-1)-1198

G. J. Sellers, A. C. Anderson, and H. K. Birnbaum
The Anomalous Heat Capacities of Niobium and Tantalum below L K
Physics Review B10, 2771-2776 (1974)
Supported by the U.S. Energy Research and Development Administration under Contract AT(11-1)-1198 and the National Science Foundation under Grant GH-33634

R. F. Mattas and H. K. Birnbaum
Isotope Effects on the Motion of O-H Clusters in Nb
Acta Metallurgica (submitted to)
Supported by the U.S. Energy Research and Development Administration under Contract AT(11-1)-1198

M.S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses: (01 07 74 - 30 06 75)

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 M. Lenahan, Research Assistant
Robert S. Shalvoy, Research Assistant
Patricia A. Birnbaum, MM College Fellow

Objectives: To measure the diffusivity of hydrogen in dilute solution in niobium and to determine the effects of oxygen and nitrogen on the hydrogen jump frequency. Knowledge of hydrogen diffusion and trapping is important to many possible uses of niobium as a shielding or cladding material in hydrogen bearing or aqueous environments.

Nuclear relaxation is also being measured in crosslinked polymeric solids. As an important measure of molecular segmental motion this should correlate with the time and temperature dependent mechanical properties of these solids and contribute to the interpretation of mechanical properties in terms of molecular structure.

Approach: Field ion microscopy has been used to study precipitation in CuBe alloys with nuclear magnetic resonance techniques which are also used for the study of hydrogen diffusion in metals and polymer network properties.

Progress: (01 07 74 - 30 06 75) The precipitation of CuBe from a Cu-2 wt % Be age hardening alloy was followed using nuclear magnetic resonance to monitor the matrix composition. Field ion microscopy was used to corroborate particle size estimates and show that lattice

distortion surrounding the precipitate particles appreciably diminished the resonance amplitude.

A variable temperature, single coil rig capable of T_1 measurements by the tone burst technique is nearing completion. Data will be used to determine the jump frequency of hydrogen diffusing in niobium. Progress in specimen preparation also has been made.

Relaxation time T_1 has been measured as a function of temperature for several specimens of polybutadiene differing in crosslink density. Sample preparation problems have been overcome and clean, chemically well-characterized samples are now yielding systematic data.

Publications: (01 07 74 - 30 06 75)

T. J. Rowland
A ^{14}N Nuclear Relaxation Study of Hydrogen Bonding in Diethylamine-Alcohol Solutions
Journal of Chemical Physics (submitted to)
Supported by the U.S. Energy Research and Development Administration under Contract AT(11-1)-1198

M.S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses: (01 07 74 - 30 06 75)

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
J. Lawrence Nelson, Research Assistant

Objectives: The fact that stress-corrosion cracking (SCC) has become a familiar and costly occurrence during the past few decades stems in part from lack of basic understanding of stress-corrosion phenomena, and, in broad terms, the object of this research is to provide mechanistic insight into the problem. Specifically, it has become focused on those failures which are thought to result from the entry of cathodically-generated hydrogen into the lattice. The view that hydrogen is responsible for a large number of stress-corrosion failures is still highly controversial and part of our effort is directed towards providing evidence for the hydrogen model. A second objective is to answer the numerous important questions related to the propagation of stress-corrosion cracks--is cracking continuous or discontinuous; if the latter, how far does the crack advance per propagation event and what is the frequency of crack advance; what is the orientation of the fracture surfaces?

Approach: Fracture tests and studies of crack propagation by means of acoustic emission sensors are used with electron diffraction and electron microprobe examination of fracture surfaces.

Progress: (01 07 74 - 30 06 75) Studies of the transgranular SCC of an Mg-Al alloy in aqueous chloride - chromate solutions have demonstrated that the failure is due to hydrogen absorption. Work on this system was discontinued in FY75, and attention was focused on α-phase Ti alloys and Al-Zn-Mg alloys, both of which undergo SCC in aqueous chloride solutions. In the case of Ti alloys, fractographic and acoustic-emission studies are in progress to compare the characteristics of crack propagation for specimens undergoing slow crack growth in either the aqueous solutions or in dry gaseous hydrogen. Results to date support the view that the mechanism of embrittlement is the same in both environments. The most interesting result for the Al-Zn-Mg alloys was that limited amounts of discontinuous cleavage can occur during tensile testing in aqueous chlorides, laboratory air and in several other moist gases. This type of failure was not observed in tests at high strain rates or in dry gases, suggesting that cleavage results from the entry of hydrogen generated by reaction of water with aluminum. Limited studies on a type-304 stainless steel yielded the interesting new result that slow crack growth occurs when the alloy is stressed in gaseous hydrogen. Significantly, the resulting fracture surfaces were similar in appearance to those produced by the transgranular SCC of this material in hot aqueous chlorides.

Publications: (01 07 74 - 30 06 75)

D. G. Chakrapani and E. N. Pugh
The Transgranular SCC of a Mg-Al Alloy:
Crystallographic, Fractographic and Acoustic-Emission Studies
Metallurgical Transactions 6A, 1155-1163 (1975)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

J. A. Beavers, H. Gabel, J. B. Woodhouse and E. N. Pugh
The Structure and Composition of Thick Tarnish Films on
Alpha-Phase Copper Alloys
Corrosion (submitted to)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198 and the Army Research Office Contract D-G127

D. G. Chakrapani and E. N. Pugh
On the Fractography of Transgranular Stress-Corrosion Failures in a Mg-Al Alloy
Corrosion (submitted to)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

D. G. Chakrapani and E. N. Pugh
On the Mechanism of SCC in a Mg-Al Alloy
Proceedings of Sixth International Congress on Metallic Corrosion (submitted to)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

D. G. Chakrapani and E. N. Pugh
Hydrogen Embrittlement in a Mg-Al Alloy
Metallurgical Transactions (submitted to)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

J. L. Nelson and E. N. Pugh
The Occurrence of Transgranular Cleavage-Like Fracture in an
Al-Zn Alloy During Tensile
Metallurgical Transactions (submitted to)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

M.S. Theses: (01 07 74 - 30 06 75)

Howard Gabel (E. N. Pugh, Adviser)
An Electron Microprobe Study of the Composition of Tarnish Films
on Copper-Zinc, Copper-Aluminum and Copper-Nickel Alloys
January 1974 (omitted from last year's report)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198 and by the Army Research Office (Durham)

Ph.D. Theses: (01 07 74 - 30 06 75)

D. G. Chakrapani (E. N. Pugh, Adviser)
Transgranular Stress-Corrosion Cracking of a Magnesium-Aluminum Alloy
May 1975
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

Interstitial Solid Solutions

Principal Investigator: Carl J. Altstetter, Sc.D.
Professor of Physical Metallurgy; Acting Head,
Department of 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

Objectives: The study of bcc refractory metals is undertaken because their attractive high temperature, corrosion and nuclear properties make them candidates for future fission and fusion reactor structural materials. We are investigating their basic physical metallurgy and, in particular, their solid solutions with the atmospheric gases, which can cause severe degradation of properties. Of equal importance is their relatively high solubility for these gases, so that they make ideal models from which much can be learned about bcc metal - interstitial solute interactions - solubility, ordering, precipitation, mechanical properties, etc. We study, to a large extent, oxygen and nitrogen in the group V metals (V, Nb and Ta). Three projects are underway: a) work hardening in vanadium containing dispersions of $V_{16}N$ platelets (mechanical properties, electron microscopy), b) thermodynamic properties and solubility of oxygen in vanadium and in β-V_9O (emf of solid galvanic cells), c) effect of solute and precipitate distributions on sputtering by energetic ions (ion beam irradiation, weight loss, scanning electron microscopy, Auger spectroscopy).

Approach: Electron microscopy and tensile tests are used for studies of work hardening. High temperature measurement of the electromotive force of solid electrolyte cells in controlled atmospheres is used to

determine thermodynamic properties. Effects of sputtering on surfaces are studied through weight loss and surface examination by electron and Auger scanning microscopy.

Progress: (01 07 74 - 30 06 75) a) The study of dispersion strengthening has been completed. There have been three major accomplishments: derivation and application of expressions for quantitative electron metallography of thin foils containing large platelet precipitates. Verification for the first time of Ashby's theory of work hardening in a bcc dispersion strengthened material. Demonstration of basic differences in dislocation-particle interactions in fcc and bcc matrices. b) The emf technique has been successfully extended from the Nb-O and Ta-O to the more complicated V-O system. Preliminary data have been obtained. c) The ion accelerator is nearly assembled. Preliminary experiments have been done on existing equipment, with good reproduction of published results.

Publications: (01 07 74 - 30 06 75)

None

M.S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses: (01 07 74 - 30 06 75)

None

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 (On leave FY 75)

Junior Staff: Robert W. Levis, Research Assistant
Theodore R. Wilken, Research Assistant

Objectives: To study alloys of the metals V, Nb and Ta with the interstitials hydrogen and carbon. Both the solid solutions of hydrogen and deuterium in these metals are to be investigated and the properties of the hydrides and deuterides. The characteristics of carbides of V and Nb in these metals is to be examined by electron microscopy, especially of the mixed carbides such as $V_xTi_yC_z$ and $V_xCr_yC_z$. The strengthening effects of these carbides will be determined. These studies are basic metallurgical studies of the thermodynamic, kinetic and crystallographic features of these alloys. Since these metals are likely candidates for structural members of nuclear and fusion reactors, they are related to practical applications of the alloys.

Approach: Tensile tests, electron microscopy, magnetic susceptibility measurements, measurement of elastic constants and determination of phase diagrams are primary techniques.

Progress: (01 07 74 - 30 06 75) (1) We have determined rates of formation of hydrides and deuterides in Ta and V. Small amounts of oxygen have been found to retard, greatly, formation rates of these compounds. Thermodynamic and kinetic parameters seem well established

for the Ta-H and Ta-D systems as well as for these binaries with 1% of oxygen present. For vanadium, our own results are internally consistent, but differ somewhat from those of Westlake at Argonne. (2) We have completed an initial study of the carbides formed in the ternary system V-Ti-C. The mixed carbide forms small thin platelets on the (310) planes of the metal. They are stable to temperatures over 1000°C, whereas similar platelike carbides in the V-C binary alloys become unstable above 400°C. (3) Initial stages of work involving tungsten will be completed.

Publications: (01 07 74 - 30 06 75)

H. Y. Chang, R. K. Viswanadham and C. A. Wert
Age Hardening in the V-C and Nb-C Systems
Metallurgical Transaction 5, 1907-1917 (1974)
Supported by the U.S. Energy Research and Development Administration under Contract AT(11-1)-1198

H. Y. Chang and C. A. Wert
Precipitation of Carbides in Deformed Vanadium
Metallurgical Transaction 5, 1671-1676 (1974)
Supported by the U.S. Energy Research and Development Administration under Contract AT(11-1)-1198

Philippe Lecocq and Charles Wert
Equilibrium in Hydride Formation in Tantalum
Thin Solid Films 25, 77-84 (1975)
Supported by the U.S. Energy Research and Development Administration under Contract AT(11-1)-1198

M.S. Theses: (01 07 74 - 30 06 75)

T. Wilkin (C. A. Wert, Adviser)
The Morphological Structures Produced During Reduction of Blue Tungsten Oxide to Tungsten Metal
May 1975
Supported by the U.S. Energy Research and Development Administration under Contract AT(11-1)-1198

Ph.D. Theses: (01 07 74 - 30 06 75)

Philippe Lecocq (C. A. Wert, Adviser)
The Solubility of Hydrogen in Tantalum
October 1974
Supported by the U.S. Energy Research and Development Administration
under Contract AT(11-1)-1198

Deformation of Intermetallic Compounds at Elevated Temperatures

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
Michael H. Loretto, Visiting Research Professor (5/21-7/20/75)

Junior Staff: Scott E. Hughes, Research Assistant
Nestor J. Zaluzec, Research Assistant

Objectives: The object of the research program falls into two parts. In the first case, the elevated temperature deformation mechanisms of <100> crystals (hard crystals) of NiAl are being determined. The research is necessary to understand the mechanisms of deformation of the polycrystalline form of the compound. Previous work in this study has indicated that climb may be responsible for plastic deformation at elevated temperatures, and experiments involving transmission electron microscopy, measurements of lattice rotations and strain rate tests are being carried out to determine the role of climb.

The second part of the program concerns the precipitation of hydrides in refractory metals. Experiments on hydrides in Nb and Ta are being carried out, involving both hydrides precipitated in bulk form, and those in thin foil. In situ experiments are planned using a working stage developed in the MRL. When appropriate stages are ready, in situ straining tests will be performed to study crack tip processes of pre-charged Nb-H alloys. The results will be related to hydrogen embrittlement.

Approach: The primary technique is the use of the transmission electron microscope for observation of specimens strained in situ.

Progress: (01 07 74 - 30 06 75) On the work on NiAl, two important results have been achieved. Firstly, we have made a detailed study of the dislocations in deformed hard crystals. Three types of Burgers vectors have been observed, namely $\underline{b}$ = <100>, <110> and <111>. We have determined that those with $\underline{b}$ = <110> and <111> are formed by the interaction of appropriate dislocations with $\underline{b}$ = <100>. We conclude that these dislocations do not contribute to plastic deformation. Secondly, we have made a determination of the plane containing the Burgers vector and the line direction of many dislocations with $\underline{b}$ = <100> and have discovered that many have no rational slip planes. These observations are consistent with climb as a mechanism of plastic deformation.

Regarding the precipitation of hydrides, we have observed that the hydride of Nb precipitated in thin foil has an ordered structure. Transmission electron microscopy has revealed that the precipitation of the hydride of Ta is accompanied by the punching of a number of prismatic dislocation loops. These loops have been analyzed and it is found that they are interstitial in nature. This is consistent with the fact that the hydride precipitation involves an expansion of the lattice.

Publications: (01 07 74 - 30 06 75)

Hamish L. Fraser and Ian P. Jones
A Note on the Increase in Usable Foil Thickness in Scanning Transmission Electron Microscopy
Philosophical Magazine 31, 225-228 (1975)
Supported by the U.S. Energy Research and Development Administration under Contract AT(11-1)-1198

Nestor J. Zaluzec and Hamish L. Fraser
The Origin of Dislocation with $\underline{b}$ = <110> in Single Crystals of β-NiAl Compressed Along <001> at Elevated Temperatures
Scripta Metallurgical 8, 1049-1054 (1974)
Supported by the U.S. Energy Research and Development Administration under Contract AT(11-1)-1198

M.S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses: (01 07 74 - 30 06 75)

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

Objectives: To develop realistic models of matrix behavior at small strains in composite crystalline materials and provide information applicable to the design of technological materials containing nondeforming phases. A central question in regard to the strength and ductility of these materials is the nature of the matrix interaction with the nondeforming phase during straining and the significance of the spacing of the latter. This is being studied in a Ni_3Al-Ni_3Nb aligned eutectic alloy, with the important features that interlamellar spacing can be varied and it can be thinned for electron microscopy.

Approach: Stress-strain determinations are combined with transmission electron microscope observation.

Progress: (01 07 74 - 30 06 75) In this period, we expect significant results on the Ni_3Al-Ni_3Nb system at several interlamellar spacings including microyielding and macroyielding tests in tension at several temperatures and dislocation structure observations after suitable strains. These are expected to provide data for the identification of the appropriate type of model for the interaction of the matrix with the reinforcing phase (e.g., plastic constraint) and for critical evaluation of specific models. Information on the intrinsic stress-strain behavior and dislocation structures of the Ni_3Al matrix phase is available from single crystal studies by other researchers.

Publications: (01 07 74 - 30 06 75)

J. Zahavi and M. Metzger
Breakdown of Films and Initiation of Pits on Aluminum During Anodizing
Localized Corrosion, NACE-3, 547-555 (1974)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

M. S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses: (01 07 74 - 30 06 75)

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 Professor

Junior Staff: Michael P. Cassidy, Research Assistant
S. Chakravorty, Research Assistant (Until 4/1/75)
Jun Ichi Fujita, Research Assistant
Myung-Hwan Kim, Research Assistant

Objectives: Solid state phase transformations of the martensitic type are being studied with emphasis on pretransformation lattice instabilities and phase nucleation, materials properties and mechanisms of the shape memory effect, and the crystallography of hydride formation in metals. The first program deals with understanding and hopefully controlling phase nucleation. The second involves a study of material properties as related to the feasibility of the shape memory effect in the direct conversion of heat into mechanical work. The third attempts to define the mechanism of hydride formation, a phenomenon of current interest for possible energy storage devices. Both bulk materials and thin films prepared by sputtering, evaporation, and thinning are examined through physical properties measurements and electron microscopy and diffraction analysis.

Approach: Vacuum evaporation and sputtering are used for preparation of thin films. Electron diffraction and transmission electron microscopy are primary tools for determination of structure and observation of nucleation, growth and phase changes.

Progress: (01 07 74 - 30 06 75) Further research has led to a more detailed understanding of "memory" alloys and the shape memory effect, with particular emphasis on thermodynamics. Temperature regimes for thermoelastic behavior and the effects of applied stress have been documented. An efficiency analysis of "solid state engines" based on the shape memory effect has been carried out, and the first approximation indicates that efficiencies as high as 20% may be possible for the direct conversion of heat into mechanical work via the shape memory effect. This effect may be of future technological significance.

Both electron diffraction and transmission electron microscopy have been used to study pretransformation "anticipation" phenomena in a number of materials which undergo martensitic transformations at lower temperatures. Qualitative observations of the intensification of lattice oscillations as the transformation temperature is approached have been made both by transmission imaging and broadening effects in electron diffraction. Crystallographic features of the lattice instabilities have been related to the geometry of the Bain strain of martensitic transformations, and may eventually be related to the (nor classical) mode of nucleation in martensites.

It has been established that hydrides in vanadium possess many of the features of martensitic transformations. Of particular interest are the regular arrays of transformation dislocations which comprise the parent-hydride interface and make for a very mobile interphase linkage. This focuses on the importance of certain types of dislocations which allow one phase to grow (and in a reversible manner) at the expense of another.

Publications: (01 07 74 - 30 06 75)

G. P. Asselin and C. M. Wayman
Nucleation and Growth on Tungsten Films Evaporated on NaCl
Physica Status Solidi (a) 24, 675-690 (1974)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

T. P. Darby and C. M. Wayman
Growth of Gold Films on Air- and Vacuum-Cleaved Molybdenite
Physica Status Solidi (a) 25, 585-590 (1974)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

T. P. Darby and C. M. Wayman
Nucleation and Growth of Gold Films on Graphite I:
Effects of Substrate Condition and Evaporation Rate
Journal of Crystal Growth 28, 41-52 (1975)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

T. P. Darby and C. M. Wayman
Anomalous Diffraction Doublet from Gold Films on Graphite Substrates
Philosophical Magazine 30, 1171-1175 (1974)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

H. C. Tong and C. M. Wayman
Thermodynamics of Thermoelastic Martensitic Transformations
Acta Metallurgica 23, 209-215 (1975)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198 and by the Army Research Office (Durham)

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)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198 and by the National Science Foundation

H. C. Tong and C. M. Wayman
Characteristic Temperatures and Other Properties of Thermoelastic Martensites
Acta Metallurgica 22, 887-896 (1974)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198 and by the National Science Foundation

H. C. Tong and C. M. Wayman
Direct Evidence of Pretransformation Lattice Instabilities
Physical Review Letters 32, 1185-1188 (1974)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

H. C. Tong and C. M. Wayman
A Simplified Calorimeter for Determining Latent Heats of
Martensitic Transformations at Low Temperatures
Metallurgica Transactions 5, 1445 (1974)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198 and by the Army Research Office (Durham)

C. M. Wayman
Shear Transformations and Microstructure
Metallography 8, 105-130 (1975)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198 and by the Army Research Office (Durham)

C. M. Wayman and T. P. Darby
Nucleation and Growth of Gold Films on Graphite II:
The Effect of Substrate Temperature
Journal of Crystal Growth 28, 53-67 (1975)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

C. M. Wayman
Martensitic Transformations: Electron Microscopy and Diffraction Studies
Modern Diffraction and Imaging Techniques in Materials Science (submitted to)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

M.S. Theses: (01 07 74 - 30 06 75)

Yue-Kong Au (C. M. Wayman, Adviser)
Some Electrical Properties of Amorphous Germanium, Indium
Antimonide and Gallium Antimonide Films
August 1974
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

M. Cassidy (C. M. Wayman, Adviser)
An Electron Microscopy Study of the Substructure of β-Hydride in Vanadium
May 1975
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

Ph.D. Theses: (01 07 74 - 30 06 75)

S. Chakravorty (C. M. Wayman, Adviser)
Crystallography of the Thermoelastic Martensitic Transformation in Ni-Al Alloys
May 1975
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

Thomas P. Darby (C. M. Wayman, Adviser)
Nucleation and Growth of Gold Thin Films Vapor Deposited
on Single Crystal Graphite Substrates
May 1974 (omitted from last years report)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

Physics of Refractory Materials

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

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

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

Junior Staff: Jim Bethin, Research Assistant (Ceramics)
Marvin W. Johnson, Research Assistant (Physics)
Michael Kolber, NIH Trainee (Physics)
Subhash Kulkarni, Research Assistant (Metallurgy) (Term 1/20/75)

Objectives: To characterize the thermal, mechanical and electrical properties of selected ceramic materials, especially the transition-metal carbides, and to interpret these properties in terms of the electronic structure of the material. Recently the program has expanded to include studies of biological ceramics, bone and teeth. The general flavor of the program is interpretive: how can the extreme hardness of these materials, for example, be explained in terms of the details of the crystal bonding and information on dislocation properties? The object is to put solid state physics in the role of explaining the behavior of complex, real materials by using and extending the sophisticated and quantitative treatments of simple solids which represent limiting cases. Such interpretation is necessary for designing new refractory materials and understanding failure of existing ones. These considerations are of considerable current importance, as new energy technologies require service under extreme conditions and appear to be materials-limited.

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*During FY 75 Professor Williams has been on leave of absence with the National Science Foundation, Division of Materials Research, Washington, D.C. However, the research has continued, being supervised by Professor Williams by monthly visits to the laboratory and via telephone and mail, and by cooperation with several other faculty members.

Approach: In association with computer calculations of electronic energy bands, measurements are made of thermal and electrical conductivity, elastic and plastic deformation. Dislocation studies use x-ray topography and surface etching.

Progress: (01 07 74 - 30 06 75) (a) With the restricted Hartree-Fock, local orbitals approach to the electronic structure of solids, we have constructed the local orbitals for TiC, calculated the charge density versus position in the crystal, and evaluated the overlap between Ti 3d and C 2p orbitals. The presence of strong, partially polar, covalent bonding between Ti and C is indicated. (b) High-temperature compression tests were initiated on samples of Co-bonded, polycrystalline carbides for comparison with previous measurements, made on the same apparatus, on carbide single crystals. Preliminary results show that up to 1100°C, the primary irreversible deformation is additional densification of the composite, whereas gross plastic deformation occurs in single crystals of the component carbides under similar conditions. (c) Dislocation velocity measurements on doped silicon single crystals using x-ray topography have been completed. For motion of both 60° edge dislocations and screw dislocations, and for both n- and p-type doping, the activation energies are lower than in intrinsic material by about half the band gap. (d) The study of large and mysterious piezoelectric signals in bent dry bone was extended to polymeric solids in hopes of finding a more uniform model material with the same property which would permit identification of the molecular origin of the effect. Of the several polymers tested, only nylon, which is hydrogen bonded, showed a piezoelectric response similar

to bent bone. (e) Studies of the etching of dental enamel by HCl, EDTA and argon ions showed that only EDTA at neutral pH attacks the boundaries rather than the cores of the enamel prisms. A reported difference in the Ca/P ratio between boundary and core by a few percent was confirmed with the electron probe.

Publications: (01 07 74 - 30 06 75)

Wendell S. Williams and Lance Breger
Analysis of Stress Distribution and Piezoelectric Response in Cantilever Bending of Bone and Tendon
Annals of the New York Academy of Science 238, 121-130 (1974)
Supported by the U.S. Energy Research and Development Administration under Contract AT(11-1)-1198

W. S. Williams, L. Breger, and M. Johnson
Ceramic Models for Study of Piezoelectricity in Organic Solids
Journal of the American Ceramic Society (submitted to)
Supported by the U.S. Energy Research and Development Administration under Contract AT(11-1)-1198

M.S. Theses: (01 07 74 - 30 06 75)

Daniel Sutherland Petty (W. S. Williams, Adviser)
Investigation of Preferential Etch Patterns Created in Human Dental Enamel During Acid Attack
October 1974
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

Ph.D. Theses: (01 07 74 - 30 06 75)

Joseph Gary Baldoni II (W. S. Williams, Adviser)
High Temperature Deformation Behavior of Cemented Carbide Cutting Tools
January 1975
Supported by the U.S. Energy Research and Development Administration under Contract AT(11-1)-1198

Lance Harris Breger (W. S. Williams, Adviser)
Piezoelectric Response of Bone and Tendon Subjected to Inhomogeneous Stress
October 1974
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

Mechanical Properties of Solids

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

Supporting Agency: National Science Foundation

Senior Staff: Jon T. Holder, Assistant Professor

Junior Staff: David M. Joncich, Research Assistant
Theodore A. Koelsh, Research Assistant
Sekyung Lee, Research Assistant
Richard J. Wallat, Research Assistant (Until 1/5/75)

Objectives: An understanding of microscopic mechanisms involved in the mechanical behavior of solids. Materials and problems of interest to both solid state physics and geophysics are considered. Principal areas of interest are: 1) elastic properties of perfect crystals and their use in estimating other properties (such as thermal properties); 2) behavior of materials containing imperfections such as point defects and dislocations.

Approach: Microscopic mechanisms are first investigated in simple systems, with application to progressively more complicated systems as that understanding grows. Generally a number of different types of measurements are carried out simultaneously on a single material, since this leads to more than a proportionate amount of information. In the investigation of the mechanical properties of ice, ultrasonic, sonic, microstrain, static stress, and dielectric techniques are used. The response of dislocations to cyclic low frequency stresses and electric fields in the 0.01 - 100 Hz range is used to determine the microscopic motions of the dislocations, and hence the mechanisms limiting plastic

flow, in ice. Macroscopic plastic behavior is also monitored with the static stress techniques in experiments on structural phase transformations in rubidium halides and in rock deformation studies. These are supplemented by acoustic emission studies in the deformation of rocks.

Progress: (01 07 74 - 30 06 75) A theoretical and experimental investigation of structural phase transformations in rubidium halides has been completed. Comparison of atomistic calculations with measurements of elastic constants and the effects of non-hydrostic stress demonstrate that: 1) the properties of the transformation can be reliably predicted by the Born model of atomic interactions; 2) phase stability does not require the vanishing of an elastic constant as has been proposed in some cases; 3) the effects of non-hydrostatic stresses can be very large, and can be estimated reliably from the atomistic calculations; and 4) thermal effects can be estimated from measured elastic properties. The success of these calculations is in contrast to previous attempts, which did not respect the model's sensitivity to input parameters and the convergence of lattice sums.

Low frequency techniques have been developed to investigate the very slow motion of dislocations in ice. Capacitive techniques for microstrain measurements in the 10^{-2} to 1 Hz range, and loaded canlilevex oscillators in the 10 - 100 Hz range have been developed.

Acoustic emission studies of deformed rock specimens have indicated that several different types of events are generated in the same type of specimen under different deformation conditions. This indicates that differences in frequency and shape of acoustic emissions can be used to

monitor mechanisms occurring during the deformation of geologic materials. Attempts being made to correlate the observed emissions with microscopic mechanisms include comparisons of the acoustic emissions results with observations of thin sections, and the investigation of effects produced by varying the conditions under which the materials are deformed (temperature, strain rate, grain size, confining pressure).

Publications: (01 07 74 - 30 06 75)

E. R. Fuller, Jr., A. V. Granato, J. Holder, and E. R. Naimon
Ultrasonic Studies of the Properties of Solids
Solid State Volume of Methods of Experimental Physics, edited by R. V. Coleman (Academic Press, 1974), Vol. II., p. 371
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198, and by the National Science Foundation

J. Holder, A. V. Granato, and L. E. Rehn
Effects of Self-Interstitials and Close Pairs on the Elastic Constants of Copper
Physical Review B 10, 363-375 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026 and by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

J. Holder, A. V. Granato, and L. E. Rehn
Experimental Evidence for Split Interstitials in Copper
Physical Review Letters 32, 1054-1057 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026 and by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

L. E. Rehn, J. Holder, A. V. Granato, R. R. Coltman, and F. W. Young, Jr.
Effects of Thermal Neutron Irradiation on the Elastic Constants of Copper
Physical Review B 10, 349-362 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026 and by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

M.S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses: (01 07 74 - 30 06 75)

Richard John Wallat (J. Holder, Adviser)
The Phase Transition of the Rubidium Halides
May 1975
Supported by the National Science Foundation under Grant DMR-72-03026

Anharmonic Effects 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
Ricardo B. Schwarz, Visiting Assistant Professor

Junior Staff: Terrell D. Berker, Research Assistant
Randall D. Isaac, Research Assistant
David L. Johnson, Research Assistant (Beginning 1/6/75)
David B. Poker, Research Assistant (Beginning 1/6/75)
David L. Read, Research Assistant (Until 1/5/75)

Objectives: We have been engaged in a program of understanding the non-linear elastic properties of materials of systematically increasing complexity. We propose now to use results previously found for materials of different bonding types and crystal structures in applications to studies of thermal properties, mechanical strength, and defects in crystals.

Approach: Ultrasonic measurement of elastic constants and determination of ultrasonic attenuation are the primary techniques.

Progress: (01 07 74 - 30 06 75) (1) Dislocation resonance was found in lead at 4.2 K in both the normal and superconducting state. (2) A theory of ultrasonic stress-bias effects was given and tested. Previously given theories were found to be invalid. (3) A method of measuring dislocation segment length distribution function was devised. (4) It was demonstrated that the force-distance profile between a dislocation and a single point defect can be determined from amplitude dependent dislocation damping measurements.

Publications: (01 07 74 - 30 06 75)

E. R. Fuller, Jr. and W. F. Weston
Relation Between Elastic-Constant Tensors of Hexagonal and Cubic Structures
Journal of Applied Physics 45, 3773-3776 (1974)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

J. A. Garber and A. V. Granato
Fourth-Order Elastic Constants and the Temperature Dependence of
Second-Order Elastic Constants in Cubic Materials
Physical Review B11, 3998-4007 (1975)
Supported by the U. S. Energy Reserach and Development Administration
under Contract AT(11-1)-1198

J. A. Garber and A. V. Granato
Theory of the Temperature Dependence of Second-Order Elastic Constants
in Cubic Materials
Physical Review B11, 3990-3997 (1975)
Supported by the U.S. Energy Research and Development Administration
under Contract AT(11-1)-1198

J. Holder, A. V. Granato, and L. E. Rehn
Experimental Evidence for Split Interstitials in Copper
Physical Review Letters 32, 1054-1057 (1974)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198 and the National Science Foundation under
Grant DMR-72-03026

J. Holder, A. V. Granato and L. E. Rehn
Effects of Interstitials and Close Pairs on the Elastic Constants
of Copper
Physical Review B10, 363-375 (1974)
Supported by the U.S. Energy Research and Development Administration
under Contract AT(11-1)-1198 and the National Science Foundation under
Grant DMR-72-03026

R. D. Isaac and R. B. Schwarz
A Simple Persistent Switch for Superconducting Solenoids
Review of Scientific Instruments 46, 638 (1975)
Supported by the U.S. Energy Research and Development Administration
under Contract AT(11-1)-1198

L. E. Rehn, J. Holder, A. V. Granato, R. R. Coltman and F. W. Young, Jr.
Effects of Thermal Neutron Irradiation on the Elastic Constants of Copper
Physical Review B10, 349-362 (1974)
Supported by the U.S. Energy Research and Development Administration
under Contract AT(11-1)-1198 and the National Science Foundation under
Grant DMR-72-03026

R. B. Schwarz and A. V. Granato
Measurement of the Dislocation-Point Defect Interaction Force-Distance Profile
Physical Review Letters (submitted to)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198 and the National Science Foundation under Grant GH-37907

K. D. Swartz, W. Bensch and A. V. Granato
The Second, Third, and Fourth Order Elastic Constants of Beta Brass
Physical Review (submitted to)
Supported by the U.S. Energy Research and Development Administration under Contract AT(11-1)-1198

W. F. Weston
Cubic and Hexagonal Single-Crystal Elastic Constants of a Cobalt-Nickel Alloy: I
Physical Review (submitted to)
Supported by the U.S. Energy Research and Development Administration under Contract AT(11-1)-1198

W. F. Weston and A. V. Granato
The Stress Dependence of the Martensitic Transformation of Cobalt-Nickel:II
Physical Review (submitted to)
Supported by the U.S. Energy Research and Development Administration under Contract AT(11-1)-1198

M.S. Theses: (01 07 74 - 30 06 75)

None

Ph.D. Theses; (01 07 74 - 30 06 75)

David Thomas Read (A. V. Granato, Adviser)
Bias Stress Detection of Dislocation Resonance in Lead
May 1975
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

6. Semiconductor Materials and Devices

Luminescence, Lasers, Carrier and Impurity Effects in Compound Semiconductors

Principal Investigator: Nick Holonyak, Jr., Ph.D.
Professor of Electrical Engineering

Supporting Agency: Advanced Research Projects Agency

Senior Staff: Nick Holonyak, Jr., Professor

Junior Staff: James J. Coleman, Research Assistant (NSF)
William R. Hitchens, Research Assistant
Michael H. Lee, Research Assistant (Until 9/13/74) and
IBM Postdoctoral Fellow (9/14/74 - 8/20/75)
Michael J. Ludowise, Research Assistant (NSF)
Ronald J. Nelson, Research Assistant
Philip D. Wright, Research Assistant

Objectives: Study III-V compounds, isoelectronic traps and complexes, spontaneous and stimulated recombination, luminescence, lasers, p-n junctions, and heterojunctions.

Approach: Crystal growth and junction formation by vapor transport, growth from solution (constant-temperature liquid-phase epitaxy, CT-LPE), and impurity diffusion. Electrical and optical measurements (4.2-300°K) on thin homogeneous samples, on p-n junctions, and on heterojunctions.

Progress: (01 07 74 - 30 06 75) A study of electron-hole recombination involving the N trap in $GaAs_{1-x}P_x$, and its optimization with crystal composition, has been accomplished in conjunction with Monsanto (M. G. Craford and co-workers) and shows that an optimum LED can be realized at $x \sim 0.65$ and not $x=1$, i.e., not as commonly believed in GaP. Quaternary layers of $In_{1-y}Ga_yP_{1-z}As_z$ have been grown successfully by liquid phase epitaxy (LPE) on VPE $GaAs_{1-x}P_x$. The resulting single heterojunction devices have permitted diode laser operation of $GaAs_{1-x}P_x$ to much higher energies (2.00 eV, λ=6200 Å) than formerly and permit direct observation (77 to 4.2 °K)

of the effect of indirect-gap (X) donor states in a composition range ($x = 0.42 - 0.43$) much closer to the direct-indirect transition ($x \equiv x_c \approx 0.46$, 77°K) than has been possible previously. These results affect the design of the most widely used LED, direct-gap $GaAs_{1-x}P_x$. In the InGaPAs/GaAsP single heterojunctions of this work, for the first time the N isoelectronic trap in $GaAs_{1-x}P_x$ (NN-pairs and A-line) has been operated in stimulated emission in a current-driven structure. These results show that resonance enhancement at $E_N \sim E_\Gamma$ does not occur and that the N trap tends to make direct-gap $GaAs_{1-x}P_x$ quasi-indirect. On the other hand, resonance-antiresonance behavior, and some tendency for quenching of laser operation, does occur when the N trap is located just above the direct (Γ) band edge or just below the band edge in donor tail states. Thus, $GaAs_{1-x}P_x$:N represents a new system in which to observe the resonant-antiresonant behavior of a narrow autoionizing trap state (N-trap) located in a continuum of states (conduction band or donor tail states).* For several years it has seemed that the quaternary $In_{1-x}Ga_xP_{1-z}As_z$, which is a direct-gap material extending from the yellow-green to the infrared, might be a better choice of alloy III-V semiconductor to employ for high energy laser emission (yellow) than $In_{1-x}Ga_xP$. This possibility is inherent in the fact that any increase Δx in Ga composition x that shrinks the crystal lattice can be balanced by a corresponding increase Δz in As composition z that increases the lattice constant, thus leading to a fixed lattice constant and above all a mechanism to minimize lattice defects and strains. Utilizing these notions and the usual slider-boat LPE crystal growth process, we have fabricated $In_{1-x'}Ga_{x'}P_{1-z'}As_{z'}/In_{1-x}Ga_xP_{1-z}As_z/In_{1-x'}Ga_{x'}P_{1-z'}As_{z'}$ ($x' \sim 0.66$, $z' \sim 0.005$; $x \sim 0.71$, $z \sim 0.10$) double

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*Note that much of this work has been carried out with M. Altarelli and A. B. Kunz.

heterojunction laser diodes that operate in the yellow at current densities $J<10^4 A/cm^2$ (λ~5850 Å, 77°K), or an order of magnitude lower than comparable $In_{1-x}Ga_xP$ homojunctions.

Publications: (01 07 74 - 30 06 75)

J. C. Campbell, N. Holonyak, Jr., M. G. Craford, and D. L. Keune
Band Structure Enhancement and Optimization of Radiative Recombination in $GaAs_{1-x}P_x$:N (and $In_{1-x}Ga_xP$:N)
Journal of Applied Physics 45, 4543-4553 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation under Grant GH-33771

J. C. Campbell, N. Holonyak, Jr., M. H. Lee, and A. B. Kunz
Recombination Processes Involving Zn and N in $GaAs_{1-x}P_x$
Physical Review B 10, 1755-1757 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the National Science Foundation under Grants DMR-72-03026 and GH-33771, and by the Aerospace Research Lab under Contract F-33615-72-C-1506

J. J. Coleman, W. R. Hitchens, N. Holonyak, Jr., M. J. Ludowise, J. O. Groves, and D. L. Keune
Liquid Phase Epitaxial $In_{1-x}Ga_xP_{1-z}As_z/GaAs_{1-y}P_y$ Quaternary (LPE)-Ternary (VPE) Heterojunction Lasers (x~0.70, z~0.01, y~0.40; λ<6300 Å, 77°K)
Journal of Applied Physics Letters 25, 725-727 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation under Grant DMR-72-03045-A01

J. J. Coleman, N. Holonyak, Jr., A. B. Kunz, W. O. Groves, D. L. Keune, and M. G. Craford
Resonant Enhancement (?) of the Recombination Probability at the Nitrogen-Tray, Γ-Band Edge Crossover in $GaAs_{1-x}P_x$:N($E_N=E_\Gamma, x=x_N$)
Solid State Communications 16, 319-322 (1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the National Science Foundation under Grants DMR-72-03026 and DMR-72-03046-A01, and by the Aerospace Research Lab under Contract F-33615-72-C-1506

J. J. Coleman, N. Holonyak, Jr., M. J. Ludowise, A. B. Kunz, M. Altarelli, W. O. Groves, and D. L. Keune
Index Dispersion Above the Fundamental Band Edge in Nitrogen-Doped $GaAs_{1-y}P_y$ (y=0.38, $E_N>E_\Gamma$)
Physical Review Letters 33, 1566-1569 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the National Science Foundation under Grants DMR-72-03026 and DMR-72-03045-A01, and by the Aerospace Research Lab under Contract F-33615-72-C-1506

J. J. Coleman, N. Holonyak, Jr., M. J. Ludowise, P. D. Wright, W. O. Groves, and D. L. Keune
Liquid Phase Epitaxial $In_{1-x}Ga_xP_{1-z}As_z/GaAs_{1-y}P_y$ Heterojunction Lasers
IEEE Journal of Quantum Electronics QE-11, (1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation under Grant DMR-72-03045-A01

J. J. Coleman, N. Holonyak, Jr., M. J. Ludowise, P. D. Wright, W. O. Groves, D. L. Keune, and M. G. Craford
Heterojunction Laser Operations of N-Free and N-Doped $GaAs_{1-t}P_y$ (y=0.42-0.43, λ~6200 Å, 77°K) Near the Direct-Indirect Transition ($y \sim y_c \simeq 0.46$)
Journal of Applied Physics 46, (1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation under Grant DMR-72-03045-A01

W. R. Hitchens, N. Holonyak, Jr., M. H. Lee, and J. C. Campbell
Liquid Phase Epitaxial Growth and Photoluminescence Characterization of Laser-Quality (100) $In_{1-x}Ga_xP$
Journal of Crystal Growth 27, 154-165 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

W. R. Hitchens, N. Holonyak, Jr., M. H. Lee, and J. C. Campbell
$In_{1-x}Ga_xP$ ($x \simeq 0.63$) Yellow Injection Laser (λ = 5900 Å, 77°K) Grown by the Method of Liquid Phase Epitaxy
Phys. Tekh. Poluprovo. 8, 2418-2424 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

W. R. Hitchens, N. Holonyak, Jr., M. H. Lee, J. C. Campbell, J. J. Coleman, W. O. Groves, and D. L. Keune
Liquid Phase Epitaxial (LPE) Grown-Junction $In_{1-x}Ga_xP$($x \sim 0.63$) Laser of Wavelength λ~5900 Å (2.10 eV, 77°K)
Applied Physics Letters 25, 352-354 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the National Science Foundation under Grant GH-33771, and by the U.S. Army Night Vision Laboratory under Contract DAAK-02-72-C-0076

M. H. Lee, N. Holonyak, Jr., W. R. Hitchens, J. C. Campbell, and M. Altarelli
The Direct-Indirect Transition in $In_{1-x}Ga_xP$
Solid State Communications 15, 981-985 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the National Science Foundation under Grant GH-33771, by the U.S. Army Night Vision Laboratory under Contract DAAK-02-72-C-0076, and by the Army Research Office under Contract DAHC-04-74-C-0005

M. H. Lee, N. Holonyak, Jr., R. J. Nelson, D. L. Keune, and W. O. Groves
Lifetime Spectra (77°K) of Nitrogen-Doped $GaAs_{1-x}P_x$
Journal of Applied Physics 46, 1290-1298 (1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation under Grant DMR-72-03045-A01

M. H. Lee, N. Holonyak, Jr., R. J. Nelson, D. L. Keune, and W. O. Groves
Behavior of Carrier Lifetime Spectra (77°K) in $GaAs_{1-x}P_x$
Journal of Applied Physics 46, 323-331 (1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation under Grant GH-33771

V. A. Voronin, W. D. Stewart, Jr., G. W. Marshall, J. B. Wagner, Jr., H. M. Macksey, and N. Holonyak, Jr.
A Scanning Electron Microscope Study of $In_{1-x}Ga_xP$
Journal of the Electrochemical Society 121, 1657-1661 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation under Grants GH-33634 and GH-33771

N. Holonyak, Jr.
American Scientist 62, 614 (1974), book review, Negative Electron Affinity Devices by R. L. Bell (Oxford University Press, London, 1973), 148 pp.
Non-MRL support

J. J. Coleman, N. Holonyak, Jr., M. J. Ludowise, R. J. Nelson, P. D. Wright, W. O. Groves, D. L. Keune, and M. G. Craford
Heterojunction Laser Operation of $GaAs_{1-x}P_x$:N on NN-Pair (E_{NN}) and A-Line (E_N) Transitions near the Direct (Γ) Band Edge
Journal of Applied Physics (submitted to)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation under Grant DMR-72-03045-A01

M. G. Craford and N. Holonyak, Jr.
The Optical Properties of the Nitrogen Isoelectronic Trap in $GaAs_{1-x}P_x$
Optical Properties of Solids: New Developments, edited by B. O. Seraphin (North-Holland Publishing Co., Amsterdam, 1975), Chapter 5
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

W. R. Hitchens, N. Holonyak, Jr., M. H. Lee, and J. C. Campbell
Liquid Phase Epitaxial (LPE) $In_{1-x}Ga_xP$ ($x\sim0.63$) Junction Laser in the Yellow Spectral Region ($\lambda\sim5900$ Å, 2.10 eV, 77°K)
Applied Physics Letters (submitted to)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation under Grant GH-33771

W. R. Hitchens, N. Holonyak, Jr., P. D. Wright, and J. J. Coleman
Low Threshold LPE $In_{1-x'}Ga_{x'}P_{1-z'}As_{z'}/In_{1-x}Ga_xP_{1-z}As_z/In_{1-x'}Ga_{x'}P_{1-z'}As_{z'}$ Yellow Double Heterojunction Laser Diodes ($J<10^4 A/cm^2$, $\lambda\approx5850$ Å, 77°K)
Applied Physics Letters (submitted to)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation under Grant DMR-72-03045-A01

M.S. Theses: (01 07 74 - 30 06 75)

Phillip Douglas Wright (N. Holonyak, Jr., Adviser)
Spectral Properties of Gallium Arsenide Phosphide Single Heterojunction Lasers
May 1975
Supported by the Advanced Research Projects Agency under Contract
DAHC-15-73-G10, by the National Science Foundation under Grant
DMR-72-03045-A01, and by the University Industrial Affiliates Program

Ph.D. Theses: (01 07 74 - 30 06 75)

Michael H. Lee (N. Holonyak, Jr., Adviser)
Lifetime Spectra of Gallium Arsenide Phosphide and Nitrogen-Doped
Gallium Arsenide Phosphide
October 1974
Supported by the Advanced Research Projects Agency under Contract
DAHC-15-73-G10, by the National Science Foundation under Grants GH-33634
and GH-33771, by the U.S. Army Night Vision Laboratory under Contract
DAAK-02-72-C-0076, and by the University Industrial Affiliates Program

Properties of Recombination Centers in Semiconductors

Principal Investigator: Chih-Tang Sah, Ph.D.
Professor of Electrical Engineering and of Physics

Supporting Agency: Advanced Research Projects Agency

Senior Staff: Chih-Tang Sah, Professor
Soong-Hak Lee, Visiting Research Assistant Professor
(Until 1/14/75)
Arnost Neugroschel, Visiting Research Associate
K. Y. Tsao, Visiting Research Associate

Junior Staff: Chak Lun Chie, Research Assistant
Hang H. Lai, Research Assistant
Thomas Y. Lo, Research Assistant
Alan R. Stivers, Research Assistant
Joseph T. Walas, Research Assistant

Objectives: The energy level schemes of and the macroscopic thermal, optical and Auger capture and emission rates of electrons and holes at imperfection centers in semiconductors are determined experimentally. These parameters are used to predict the electrical and optical properties of silicon diodes, transistors, integrated circuits and compound semiconductor devices. Quantum mechanical theories are developed to interpret these parameters.

Approach: These macroscopic parameters are measured by observing the transient current and capacitance of the depletion layer of a semiconductor diode after the diode is switched electrically, optically or thermally. Quantum mechanical calculations of these recombination-generation-trapping parameters are made using the impurity pseudopotential model with and without adjustable parameters.

Progress: (01 07 74 - 30 06 75) Detailed experimental investigations have been undertaken on the properties of Cr and Ta as impurity centers in silicon

by doping during crystal growth. High concentrations of these centers (1 atomic percent) can be introduced but only a few part per billion are electrically active. Electron and hole mobilities are substantially reduced due to the high concentration of the inactive centers. The recombination centers induced by a highly strained surface layer reported previously are studied further to determine their concentration profile in the diffused layer. The diffused profile with a U shape is a critical parameter in the determination of the injection efficiency of silicon p-n junctions and transistors not recognized previously. Experiments are in progress to study the electrically active centers due to radiation damage in silicon exposed to MeV proton beams to further the understanding of recombination centers introduced during ion implantation of silicon integrated circuits.

Publications: (01 07 74 - 30 06 75)

Karl Hess, Arnost Neugroschel, C. C. Shiue, and C. T. Sah
Nonohmic Electron Conduction in Silicon Surface Inversion Layers at Low Temperatures
Journal of Applied Physics 46, 1721-1727 (1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the Air Force Office of Scientific Research under Contract AFOSR-71-2067, and by the National Science Foundation under Grant GK-30283

K. Hess and C. T. Sah
Dipole Scattering at the Si-SiO_2 Interface
Surface Science 47, 650-654 (1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the Air Force Office of Scientific Research under Contract AFOSR-71-2067, and by the National Science Foundation under Grant GK-30283

Karl Hess and C. T. Sah
Warm and Hot Carriers in Silicon Surface Inversion Layers
Physical Review 10, 3375-3386 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the Air Force Office of Scientific Research under Contract AFOSR-71-2067, and by the National Science Foundation under Grant GK-30283

M. J. McNutt and C. T. Sah
The Effects of Spatially Inhomogeneous Oxide Charge Distribution on the MOS Capacitance-Voltage Characteristics
Journal of Applied Physics 45, 3916-3921 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the Air Force Office of Scientific Research under Contract AFOSR-71-2067, and by the National Science Foundation under Grant GK-30283

M. J. McNutt and C. T. Sah
Experimental Observations of the Effects of Oxide Charge Inhomogeneity on Fast Surface State Density from High Frequency MOS Capacitance-Voltage Characteristics
Journal of Applied Physics Letters 26, 378-380 (1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the Air Force Office of Scientific Research under Contract AFOSR-71-2067, and by the National Science Foundation under Grant GK-30283

Sokrates T. Pantelides and C. T. Sah
Theory of Localized States in Semiconductors I: New Results Using an Old Method
Physical Review B 10, 621-637 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the Air Force Office of Scientific Research, and by the National Science Foundation under Grant GH-33634

Sokrates T. Pantelides and C. T. Sah
Theory of Localized States in Semiconductors II: The Pseudo Impurity Theory Application to Shallow and Deep Donors in Silicon
Physical Review B 10, 638-658 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the Air Force Office of Scientific Research, and by the National Science Foundation under Grant GH-33634

C. T. Sah and C. T. Wang
Experiments on the Origin of Process Induced Recombination Centers in Silicon
Journal of Applied Physics 46, 1767-1776 (1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the Air Force Cambridge Research Lab under Contract F-19628-72-C-0199

C. T. Sah, C. T. Wang, and S. H. Lee
Junction Edge Region Thermally Stimulated Capacitance (SCAP) of n-Si Doped with Phosphorus and Bismuth
Applied Physics Letters 25, 523-524 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the Air Force Cambridge Research Lab under Contract F-19628-72-C-0199

M. J. McNutt and C. T. Sah
Determination of the MOS Oxide Capacitances
Journal of Applied Physics (submitted to)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the Air Force Office of Scientific Research under Contract AFOSR-71-2067, and by the National Science Foundation under Grant GK-30283

M.S. Theses: (01 07 74 - 30 06 75)

Peter S. Bachert (M. M. McNutt, Adviser)
High-Frequency Capacitance-Voltage Analysis of MOS Surface States
January 1975
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the Air Force Office of Scientific Research under Grant AFOSR-71-2067, and by the National Science Foundation under Grant GK-30283

Ph.D. Theses: (01 07 74 - 30 06 75)

Michael John McNutt (C. T. Sah, Adviser)
Theory and Experiments on High Frequency Metal-Oxide-Semiconductor Capacitance
October 1974
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

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MATERIALS RESEARCH LABORATORY PUBLICATIONS

July 1, 1974 - June 30, 1975

1. Degenerate Quantum Systems

A. C. Anderson and S. G. O'Hara
The Lattice Conductivity of Normal and Superconducting Niobium
Journal of Low Temperature Physics 15, 323-333 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

S. Alterovitz and D. E. Mapother
Pressure Dependence of the Critical Magnetic Field of Superconducting Lead
Physical Review B11, 139-144 (1975)
Supported by the National Science Foundation under Grant GH-33634

S. Alterovitz and D. E. Mapother
Low Temperature Application for Commercial Strain Gages
Review of Scientific Instruments 45, 1528-1530 (1974)
Supported by the National Science Foundation under Grant GH-33634

Ravindra N. Bhatt and W. L. McMillan
Theory of Anomalous Dispersion in Liquid He^4
Physical Review A 10, 1591-1597 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

D. M. Ginsberg
The Depression of the Superconducting Transition Temperature Caused by Iron-Group Magnetic Impurities
Physical Review (Comments and Addenda) 10, 4044-4045 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-37980

D. M. Ginsberg and B. J. Mrstik
Electronic Part of the Thermal Conductivity of a Thin, Superconducting Film Composed of Lead and Gadolinium
Low Temperature Physics LT 13, 767-771 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GP-28996

E. L. Griffin and J. M. Mochel
Low Temperature Thin Film NiCr Thermometers
Review of Scientific Instruments 45, 1265-1267 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

R. D. Isaac and R. B. Schwarz
A Simple Persistent Switch for Superconducting Solenoids
Review of Scientific Instruments 46, 638 (1975)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

S. G. O'Hara and A. C. Anderson
The Electronic Thermal Conductivity of Strained Aluminum Below 1 K
Physica Status Solidi B 67, 401-404 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026

S. G. O'Hara and A. C. Anderson
Resonant Scattering of Thermal Phonons by Dislocations in Superconducting Aluminum
Physical Review B 9, 3730-3734 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026

S. G. O'Hara and A. C. Anderson
The Scattering of Thermal Phonons by Dislocations in Superconducting Lead and Tantalum
Physical Review B 10, 574-579 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

S. G. O'Hara, G. J. Sellers, and A. C. Anderson
The Influence of Hydrogen on the Thermal Conductivities of Superconducting Nb and Ta
Physical Review B 10, 2777-2781 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

C. J. Pethick, H. Smith, and P. Bhattacharyya
Viscosity and Thermal Conductivity of Superfluid ^{3}He: Low-Temperature Limit
Physical Review Letters 34, 643-646 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026

G. J. Sellers and A. C. Anderson
Calorimetry Below 1 K: The Specific Heat of Copper
Review of Scientific Instruments 45, 1256-1259 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

G. J. Sellers, A. C. Anderson, and H. M. Birnbaum
The Anomalous Heat Capacities of Niobium and Tantalum Below 1 K
Physical Review B 10, 2771-2776 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026 and by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

G. J. Sellers, M. Paalanen, and A. C. Anderson
The Anomalous Heat Capacity of Superconducting Vanadium
Physical Review B 10, 1912-1915 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

T. E. Washburn, J. E. Rutledge, and J. M. Mochel
A Domain of Two Dimensional Excitations in Superfluid Helium Films
Physical Review Letters 34, 183-186 (1975)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-37892

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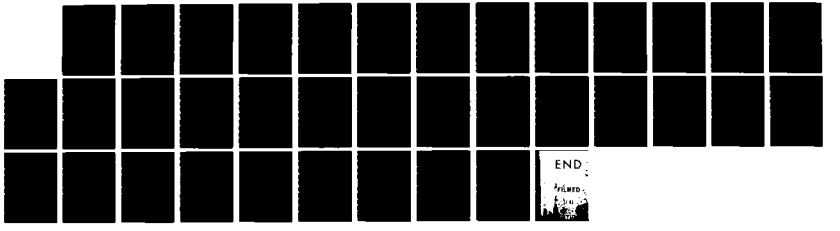

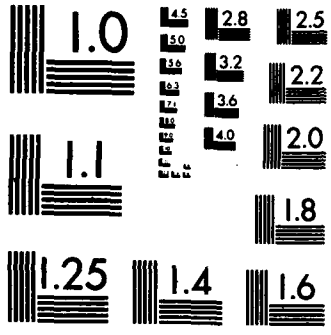

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

2. Electron-Lattice Coupling

M. A. Bowen
The Effects of Kinetic Anisotropy and Nonlocal Pseudopotentials on Thermoelectric Power
Lettere Al Nuovo Cimento 12, 151-154 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026

Marshall A. Bowen and John D. Dow
Transport of Electrons in Compressed Li, Na, and K: Thermoelectric Powers, Resistivities and Hall Coefficients
Physical Review (1975)
Supported by the National Science Foundation under Grant DMR-72-03026

James B. Boyce, Thomas J. Aton, and Charles P. Slichter
NMR Study of the Electron Spin Density Near Iron Group Atoms in Cu
Proceedings of Conference on Magnetism and Magnetic Materials 18, 252-256 (1974)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

James B. Boyce, Thomas Aton, Thomas Stakelon, and Charles P. Slichter
Spin Polarization Near Iron Group Atoms in Cu
Pure Applied Chemistry 40, 141 (1974)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

F. C. Brown
Ultraviolet Spectroscopy of Solids with the Use of Synchrotron Radiation
Solid State Physics 29, 1-73 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

A. K. Burnham, G. R. Alms, and W. H. Flygare
The Local Electric Field: I. The Effect on Isotropic and Anisotropic Rayleigh Scattering
Journal of Chemical Physics 62, 3289-3297 (1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

D. J. Chakrabarti
Effect of Atomic Ordering on the Magnetic Properties of Pd_3Mn and of Some More Dilute Pd-Mn Alloys
International Journal of Magnetism 6, 305-311 (1974)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

Y. M. Cheng, P. C. Allen, and D. Lazarus
Pressure Coefficient of Thermoelectric Power of Platinum/Platinum-10% Rhodium and Chromel/Alumel Thermocouples
Applied Physics Letters 26, 6-7 (1975)
Supported by the U. S. Energy and Research Development Administration under Contract AT(11-1)-1198

B. deMayo
Magnetism in Gold-Iron Alloys Below 14 at.%Fe
Journal of Physics and Chemistry of Solids 35, 1525-1531 (1974)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

John D. Dow
Excitons in Degenerate and Non-degenerate Semiconductors
Proceedings of the 12th International Conference of Physics Semiconductors, Stuttgart (1974), p. 957-961
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39132

John D. Dow
K-edge X-ray Spectra of Mg and Other Simple Metals: The Absence of Evidence for Orthogonality Catastrophes
Physical Review B 9, 4165-4170 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39132

J. D. Dow
X-ray Edges: Broadening Mechanisms, Selection Rules, Sum Rules, Compatibility Relationships, and Orthogonality Catastrophes
Proceedings of the Fourth International Conference on Vacuum Ultraviolet Radiation Physics 8.2, 649-661 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026

John D. Dow
X-ray Edges of Free-electron Metals: Comparison of Theory with Data
Physica Fennica 9, Suppl. 51 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39132

John D. Dow, M. Bowen, Ralph Bray, D. L. Spears, and Karl Hess
Piezo-Urbach Rule for Acoustoelectric Domains in GaAs
Physical Review B 10, 4305-4308 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39132, by GH-33344x (Purdue), and by the Advanced Research Projects Agency under Contract DAHC-0213 (Purdue)

John D. Dow and Donald R. Franceschetti
Threshold Scaling Rules for Cooperative Emission of X-rays
Physics Letters 50A, 1-2 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

John D. Dow, D. R. Franceschetti, and D. L. Smith
Inelastic Electron Scattering: Tests of Many-electron Threshold Theory
Physical Review B 11, 684-689 (1975)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39132

John D. Dow, John E. Robinson, John H. Slowik, and Bernd F. Sonntag
On the Theory of Soft-X-ray Absorption Thresholds: Amorphous Mg_xSb_{1-x} Alloys and Metallic Li, Na, Mg, and Al
Physical Review B 10, 432-447 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39132, by the Advanced Research Projects Agency under Contract HC-15-67-C-0221, and by the Army Research Office (Durham)

John D. Dow and Darryl Lyle Smith
X-ray Spectra of Metallic Alloys: Many Electron Effects
Journal of Physics F: Metal Physics 3, L170-L172 (1973)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39132 (Omitted from last year)

John D. Dow, Darryl L. Smith, and Bernd F. Sonntag
X-ray Spectra of Aluminum
Physical Review B 10, 3092-3098 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39132, and by the U. S. Army Research Office (Durham) under Contract ARO-D31-124-71-G103

John D. Dow, Lewis N. Watson, and Derek J. Fabian
On the K X-ray Emission Edge-shapes of Free-electron Metals
Journal of Physics F: 4, L76-L79 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39132

H. G. Drickamer
Exploratory Research at High Pressure
Materials Under Pressure, edited by T. Hirone (Maruzen Press Co., Tokyo, 1975) pp. 1-35
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

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
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

D. L. Fanselow and H. G. Drickamer
High Pressure Studies of the Electronic Behavior of Bianthrones
Journal of Chemical Physics 61, 4567-4574 (1974)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

C. P. Flynn
Charge Transfer Complexes in Metals
Comments on Solid State Physics 6, 1-6 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

Donald R. Franceschetti and John D. Dow
Auger Rates for Soft X-ray Transitions in Ionic, Atomic, and Metallic Lithium
Journal of Physics F: 4, L151-L155 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39132

T. L. Gilbert and A. B. Kunz
Single-Center Orbital Localization
Physical Review 10, 3706-3710 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

Dipan K. Ghosh and P. Bhattacharyya
Applications of Coherent Potential Approximations to Ni-Rich Ni-Cu Alloys
Physical Review B 11, 2642-2650 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026

N. A. Halasa, G. DePasquali, and H. G. Drickamer
High Pressure Studies of Ferrites
Physical Review B10, 154-164 (1974)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

J.-P. Hansen, I. R. McDonald, and E. L. Pollock
Statistical Mechanics of Dense Ionized Matter. III: Dynamical Properties of the Classical One-Component Plasma
Physical Review A 11, 1025-1039 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026 and by an IBM Postdoctoral Fellowship

R. S. Hockett and David Lazarus
Search for Magneto-Flicker Noise in K
Physical Review B10, 4100-4111 (1974)
Supported by the U. S. Energy and Research Development Administration under Contract AT(11-1)-1198

E. N. Koch and C. P. Flynn
Sharp Coupling Transition of Gd in AlGa Solvents
Physical Review B 10, 4071-4078 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

A. Barry Kunz
Calculation of Optical Absorption Edges and Photo-Emission Edges in Solids
Proceedings of the Conference on Vacuum UV Spectroscopy, Hamburg, Germany, 1974
Supported by the National Science Foundation under Grant DMR-72-03026 and by the Aerospace Research Lab under Contract F-33615-72-C-1506

A. Barry Kunz
Distinction Between Optical Absorption Edges and Photo-Emission Edges in Solids
Journal of Physics C 7, L231-L234 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026 and by the Aerospace Research Lab under Contract F-33615-72-C-1506

A. Barry Kunz and Daniel J. Mickish
Electronic Structure of LiH and NaH
Physical Review B 11, 1700-1704 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026, by the Advanced Research Projects Agency under Contract HC-04-69-C0007, and by the Aerospace Research Lab under Contract F-33615-72-C-1506

R. L. Marchand
Contribution of Two Phonon Processes to the Spin-Lattice Relaxation Rate of Kramers Ions
Physical Review B 9, 4613-4617 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

R. L. Marchand, G. E. Fish, and H. J. Stapleton
Spin Lattice Relaxation in Trivalent Uranium in Anhydrous Lanthanum Trichloride
Physical Review B 11, 23-26 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026

Daniel J. Mickish, A. Barry Kunz, and T. C. Collins
Optical Properties of LiF
Physical Review B 9, 4461-4467 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

Daniel J. Mickish, A. Barry Kunz, and Sokrates T. Pantelides
Electronic Structure and Optical Properties of Metallic Calcium
Physical Review B 10, 1369-1383 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026, by the Advanced Research Projects Agency under Contract HC-04-69-C0007, and by the Aerospace Research Lab under Contract F-33615-72-C-1506

S. H. Moon and H. G. Drickamer
The Effect of Pressure on Hydrogen Bonds in Organic Solids
Chemical Physics 61, 48-54 (1974)
Supported by the U. S. Energy Research and Devylopment Administration under Contract AT(11-1)-1198

B. Y. Okamoto and H. G. Drickamer
The Evaluation of Configuration Coordinate Parameters from High Pressure Optical Data I: Phenanthrene, Anthracene and Tetracene
Journal of Chemical Physics 61, 2870-2877 (1974)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

B. Y. Okamoto and H. G. Drickamer
The Evaluation of Configuration Coordinate Parameters from High Pressure Optical Data II: Purine and Pyrimidine Bases and Nucleosides
Journal of Chemical Physics 61, 2878-2882 (1974)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

B. Y. Okamoto and H. G. Drickamer
High Pressure Studies of Solvent Effects on Anthracene Spectra
Proceedings of the National Academy of Sciences 71, 4757-4759 (1974)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

B. Y. Okamoto, W. D. Drotning, and H. G. Drickamer
The Evaluation of Configuration Coordinate Parameters from High Pressure Absorption and Luminescence Data
Proceedings of the National Academy of Sciences 71, 2671-2674 (1974)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

Sokrates T. Pantelides, Daniel J. Mickish, and A. Barry Kunz
An AB INITIO Study of the Electronic Properties of Magnesium Oxide
Solid State Communications 15, 203-205 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026, by the Advanced Research Projects Agency under Contract HC-04-69-C0007, and by the Aerospace Research Lab under Contract F-33615-72-C-1506

Sokrates T. Pantelides, Daniel J. Mickish, and A. Barry Kunz
Correlation Effects in Energy-Band Theory
Physical Review 10, 2602-2613 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39811, and by the Aerospace Research Lab under Contract F-33615-72-C-1506

S. T. Pantelides, D. J. Mickish, and A. Barry Kunz
Electronic Structure and Properties of Magnesium Oxide
Physical Review B 10, 5203-5212 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39811, and by the Aerospace Research Lab under Contract F-33615-72-C-1506

D. J. Phelps, R. Avci, and C. P. Flynn
Metal-Insulator Transition in Metal-Rare Gas Alloys
Physical Review Letters 34, 23-26 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026

M. B. Salamon, J. W. Bray, G. DePasquali, R. A. Craven, G. Stucky, and A. Schultz
Thermal Conductivity of Tetrathiofulvalinium-Tetracyanoquinodimethane (TTF-TCNQ) Near the Metal-Insulator Transition
Physical Review B 11, 619-622 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026

M. B. Salamon and F. L. Lederman
Universality and the Critical Specific Heat of β-brass
Physical Review (Comments and Addenda) B 10, 4492-4494 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-33750

R. D. Shull and Paul A. Beck
Mictomagnetic to Ferromagnetic Transition in Cr-Fe Alloys
AIP Conference Proceedings 24, 95-96 (1975)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

D. S. Simons and M. B. Salamon
Specific Heat and Resistivity of Gadolinium Near the Curie Point in External Magnetic Fields
Physical Review B 10, 4680-4686 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

Charles P. Slichter
Some Scientific Contributions of Herbert S. Gutowsky
Proceedings of International Society of Magnetic Resonance 17, 274-280 (1975)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

John H. Slowik
Core Excitons in Amorphous Magnesium Alloys
Physical Review B 10, 416-431 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

B. Sonntag and Frederick C. Brown
Soft X-ray Response of Transition Metal Layer Crystals
Physical Review B 10, 2300-2306 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026, and by the U. S. Army Research Office (Durham) under Contract ARO-D31-124-71-G103

H. J. Stapleton, R. L. Marchand, and E. R. Lemar
Hyperfine Effects on Spin-Lattice Relaxation Rates of Rare Earth Salts: Theory and Experimental Data
Physical Review B 10, 2687-2696 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

R. A. Tilton and C. P. Flynn
Sharp Optical Spectra of Impurities in Metals
Physical Review Letters 34, 20-23 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026

P. B. Visscher
High Temperature Thermodynamics of the Hubbard Model: An Exact Numerical Solution
Physical Review B 10, 932-942 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

P. B. Visscher
Phase Separation in the Hubbard Model at Zero Temperature
Physical Review B 10, 943-945 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

Gregorio Weber, Fumio Tanaka, Byron Y. Okamoto, and H. G. Drickamer
The Effect of Pressure on the Molecular Complex of Isoalloxazine and Adenine
Proceedings of the National Academy of Sciences 71, 1264-1266 (1974)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

Jonathon D. Weiss and D. Lazarus
Pressure Dependence of the Thermoelectric Power of Sodium Between 5°K and 14°K
Physical Review B10, 456-473 (1974)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

Lawrence R. Whalley and Charles P. Slichter
Electric Field Gradients in Copper-Nickel Alloys
Physical Review B9, 3793-3796 (1974)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

3. Disordered Materials

G. R. Alms, T. D. Gierke, and W. H. Flygare
Depolarized Rayleigh Scattering in Liquids: The Density and Temperature Dependence of the Orientational Pair Correlations in Liquids Composed of Anisometric Molecules
Journal of Chemical Physics 61, 4083-4090 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

R. J. Ansems and C. G. Bergeron
Devitrification in Fiberglass Compositions, Part I
Glass Industry 56, (3) 16-22 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026 and by Australian Consolidated Industries Fiberglass Ltd.

R. J. Ansems and C. G. Bergeron
Devitrification in Fiberglass Compositions, Part II
Glass Industry 56, (4) 24-26 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026 and by Australian Consolidated Industries Fiberglass Ltd.

R. C. Birtcher, Y. Lwin, and J. S. Koehler
Isochronal Annealing of Pure Lead Irradiated at 1.5°K
Physical Review Letters 33, 899-900 (1974)
Supported by U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

V. M. Cheng, W. B. Daniels, and R. K. Crawford
Melting Parameters of Methane and Nitrogen from 0-10 Kilobars
Physical Review B 11, 3972 (1975)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198, and by the National Science Foundation under Grants GP-7739 and GP-18573 (University of Delaware)

K. C. Chu and W. L. McMillan
Static and Dynamic Behavior Near a Second Order Smectic A-Nematic Phase Transition by Light Scattering
Physical Review A 11, 1059-1067 (1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

W. H. Flygare, B. R. Ware, and S. L. Hartford
Electrophoretic Light Scattering
Molecular Electro-Optics, edited by C. T. O'Konski (Marcel Dekker, Inc., 1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation

C. P. Flynn
Resonance Mode Hopping and the Stage I Annealing of Metals
Thin Solid Films 25, 37-43 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

T. D. Gierke and W. H. Flygare
Depolarized Raleigh Scattering in Liquids; Molecular Reorientation and Orientation Pair Correlations in a Nematic Liquid Crystal; MBBA
Journal of Chemical Physics 61, 2231-2240 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

K. Jain, W. T. Wozniak, and M. V. Klein
Use of a Diffraction Grating to Reject Fluorescence from a Tunable Dye Laser
Applied Optics 14, 811-812 (1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation under Grant GH-37757

J. Jonas
Nuclear Magnetic Resonance at High Pressure
Annual Reviews of Physical Chemistry 26, 167-190 (1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the National Science Foundation under Grant GP-28268X, and by the U. S. Air Force Office of Scientific Research under Grant AFOSR-77-2286

Miles V. Klein
Electronic Raman Scattering
Raman Scattering in Solids, edited by Manuel Cardona (Springer-Verlag, 1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation under Grant GH-37757

J. Koehler
Decrease in the Void Growth Rate by Interstitial Trapping
Jorunal of Applied Physics 46, 2423-2427 (1975)
Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198

N.-I. Liu and J. Jonas
Pressure Effects on Molecular Motions and Glass Transition in Several Amorphous Elastomers
Journal of Magnetic Resonance 18, 465-479 (1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, and by the National Science Foundation under Grant GP-28268X

J. C. McGurk, T. G. Schmalz, and W. H. Flygare
Fast Passage in Rotational Spectroscopy: Theory and Experiment
Journal of Chemical Physics 60, 4181-4188 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

Judith G. Peascoe, W. R. Fenner, and Miles V. Klein
Raman Scattering by the Hydroxyl Ion in KCl and KBr
Journal of Chemical Physics 60, 4208-4218 (1974)
Supported by the Advanced Research Projects Agency under Contracts DAHC-15-73-G10 and HC-15-67-C-0221 and by the National Science Foundation under Grants DMR-72-03026, GH-37757, GP-11173, and GP-28319

J. L. Vorhaus and A. C. Anderson
The Low Temperature Specific Heat of Vitreous Silica Containing Hydrogen and Helium Solutes
Journal of Non-Crystalline Solids 17, 241 (1975)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-39135

D. J. Wilbur and J. Jonas
Fourier Transform NMR in Liquids at High Pressure. III. Spin-Lattice Relaxation in Toluene-d_8
Journal of Chemical Physics 62, 2800-2807 (1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, and by the National Science Foundation under Grant GP-28268X

M. P. Zaitlin and A. C. Anderson
Thermal Conductivity of Borosilicate Glass
Physical Review Letters 33, 1158-1161 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026 and GH-39135

M. P. Zaitlin and A. C. Anderson
Thermal Conductivity of Deformed Germanium Below 1 K
Physical Review B 10, 580-581 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

4. Surfaces, Interfaces, Small Particles and Catalysis

A. C. Anderson
The Kapitza Resistance and Related Phenomena
Proceedings of the European Physical Society Topical Conference on Liquid and Solid Helium, Haifa, Israel, 1974
Supported by the National Science Foundation under Grant DMR-72-03026

R. J. Blattner, J. E. Baker and C. A. Evans, Jr.
A Simple Ion Probe Attachment for Existing Mass Spectrometers
Analytical Chemistry 46, 2171-2176 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GP-33273

Theodore L. Brown
Cobalt-59 Nuclear Quadrupole Resonance Spectroscopy
Accounts of Chemical Research 7, 408-415 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026, GP-6396X and GP-30256X

Blaine H. Byers and Theodore L. Brown
Activation of Molecular Hydrogen by a Transition Metal Carbonyl Radical Species
Journal of the American Chemical Society (1975)
Supported by the National Science Foundation under Grants DMR-72-03026 and MPS-71-03201

Blaine H. Byers and Theodore L. Brown
Transition Metal Carbonyl Substitution via a Radical Chain Pathway
Journal of the American Chemical Society 97, 947-948 (1975)
Supported by the National Science Foundation under Grants DMR-72-03026 and MPS-71-03201

W. K. Chu, M-A. Nicolet, J. W. Mayer, and C. A. Evans, Jr.
Comparison of Backscattering Spectrometry and SIMS by Analysis of Ta_2O_5 Layers
Analytical Chemistry 46, 2136 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GP-33273 and by the Office of Naval Research (Cal Tech)

B. N. Colby and C. A. Evans, Jr.
Hollow-Cathode Ionization for the Mass Spectrometric Analysis of Conducting Solids
Analytical Chemistry 46, 1236-1242 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

T. C. Collins, A. B. Kunz and P. W. Deutsch
Calculation of Excitation Energies of Atomic Systems Using OAO
Physical Review A 10, 1034-1040 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

Richard L. Davison, David F. S. Natusch, John R. Wallace, and Charles A. Evans, Jr.
Trace Metals in Fly Ash: Dependence of Concentration on Particle Size
Environmental Science and Technology 8, 1107 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GI-31605-IES-7

David A. Dieterich, Iain C. Paul, and David Y. Curtin
Structural Studies of Nitrosobenzene and 2-Nitrosobenzoic Acid. Crystal and Molecular Structures of cis-Azobenzene Dioxide and trans-2,2'-Dicarboxyazobenzene Dioxide
Journal of the American Chemical Society 96, 6372-6380 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026 and a National Science Foundation Fellowship, and by the Advanced Research Projects Agency under Contract HC-15-67-C-0221

D. Michael Duggan, R. G. Jungst, K. R. Mann, G. D. Stucky and D. N. Hendrickson
Electronic and Crystallographic Study of Two Cyanide-Bridged Copper (II) Dimers. Magnetic Exchange Interactions Through a Linear Cu-CN-Cu Bridge and a Hydrogen Bonded Cu-CN...H-N-Cu System
Journal of the American Chemical Society 96, 3443-3450 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026 and by HEW PHS HL13652

Charles A. Evans, Jr.
Thin Film Compositional Analysis - A Comparison of Techniques
Journal of Vacuum Science and Technology 12, 144-150 (1975)
Supported by the National Science Foundation under Grants DMR-72-03026 and GP-42330X

J. F. Folinsbee and A. C. Anderson
The Kapitza Resistance to a Variety of Metallic Surfaces Below 0.3 K
Journal of Low Temperature Physics 17, 409-424 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

K. Hess and C. T. Sah
Dipole Scattering at the Si-SiO_2 Interface
Surface Science 47, 650-654 (1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the Air Force Office of Scientific Research under Contract AFOSR-71-2067, and by the National Science Foundation under Grant GK-30283

Karl Hess and C. T. Sah
Warm and Hot Carriers in Silicon Surface Inversion Layers
Physical Review 10, 3375-3386 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the Air Force Office of Scientific Research under Contract AFOSR-71-2067, and by the National Science Foundation under Grant GK-30283

Patrick S. Ireland, Larry W. Olson, and Theodore L. Brown
Spin Echo Double Resonance Detection of Deuterium Quadrupole Resonance Transitions in $DMn(CO)_5$
Journal of the American Chemical Society (1975)
Supported by the National Science Foundation under Grants DMR-72-03026 and MPS-71-03201

R. Jungst, D. Sekutowski and G. D. Stucky
1,3 Magnetic Exchange in Linear Trimetallic Ti(III) Complexes
Journal of the American Chemical Society 96, 8108-8109 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

Rudolph Jungst and Galen Stucky
A Mono-bridged Inner Sphere Dimer. X-ray Crystal Structure of μ-cyanobis (5,7,7,12,14,14-hexamethyl 1,4,8,11-tetraazacyclotetradeca-4,11-diene) dicopper (II) perchlorate
Inorganic Chemistry 13, 2404-2408 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

H. S. A. Kumar and C. G. Bergeron
Structural Interpretation of the Densities of Lead Borate Melts
Journal of the American Ceramic Society 57, 537-538 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

A. B. Kunz
Influence of Electron Correlation on Surface States of Nonmetallic Solids
Solid State Communications 16, 541-544 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026 and by the Aerospace Research Lab under Contract F-33615-72-C-1506

Chung-Tang Lin, David Y. Curtin, and Iain C. Paul
Use of Solid-Gas Reactions to Distinguish Between Left- and Right-Handed Single Crystals of an Enantiomeric Pai
Journal of the American Chemical Society 96, 6199 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

Chung-Tang Lin, Iain C. Paul, and David Y. Curtin
Anisotropic Reaction with Ammonia Gas of a Crystal of a Carboxylic Acid with Linear Hydrogen-Bonded Chains. An Example of Unitropic Attack
Journal of the American Chemical Society 96, 3699-3701 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

A. J. Marlor, C. G. Bergeron, and H. S. A. Kumar
X-ray Diffraction Data and Enthalpy of Fusion of $Cs_2B_6O_{10}$
Journal of the American Ceramic Society (Note) 57, 233 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026 and by the Advanced Research Projects Agency under Contract HC-15-67-C-0221

Rodger S. Miller, David Y. Curtin, and Iain C. Paul
Reactions of Molecular Crystals with Gases I. Reactions of Solid Aromatic Carboxylic Acids and Related Compounds with Ammonia and Amines
Journal of the American Chemical Society 96, 6329-6334 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

Rodger S. Miller, Iain C. Paul, and David Y. Curtin
Reactions of Molecular Crystals with Gases II. The X-Ray Structure of Crystalline 4-Chlorobenzoic Acid and the Anisotropy of its Reaction with Ammonia Gas
Journal of the American Chemical Society 96, 6334-6339 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

Rodger S. Miller, David Y. Curtin, and Iain C. Paul
Reactions of Molecular Crystals with Gases III. The Relationship of Anisotropy to Crystal Structure in Reactions of Carboxylic Acids and Anhydrides with Ammonia Gas
Journal of the American Chemical Society 96, 6340-6349 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

S. G. O'Hara and A. C. Anderson
Thermal Impedance Across Metallic and Superconducting Foils Below 1 K
Journal of Physics and Chemistry of Solids 36, 1677-1682 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

Iain C. Paul and David Y. Curtin
Reactions of Organic Crystals with Gases
Science 187, 19-26 (1975)
Supported by the National Science Foundation under Grants DMR-72-03026 and GP-34545X

Cheryl D. Pribula, Theodore L. Brown, and Eckard Munck
Calculated and Observed Field Gradients in $[M(CO)_{5-x}P_x]^n$ Complexes
Journal of the American Chemical Society 96, 4149-4154 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026, GP-6396X and GP-30256X

Wendell E. Rhine, J. Davis and Galen Stucky
Unsaturated Organometallic Compounds of the Main Group Elements. The Isolation and Structural Properties of bis[(tetramethylethylenediamine) lithium(I)] Anthracenide
Journal of the American Chemical Society 97, 2079-2086 (1975)
Supported by the National Science Foundation under Grants DMR-72-03026 and MPS-74-23000

Wendell E. Rhine and G. D. Stucky
Unsaturated Compounds of the Main Group Elements: Indenyllithium Tetramethylethylenediamine
Journal of the American Chemical Society 97, 737-743 (1975)
Supported by the National Science Foundation under Grant DMR-72-03026

D. Sekutowski, R. Jungst and G. D. Stucky
Electronic and Magnetic Properties of Linear Chain Complexes Derived from Biscyclopentadienyl Titanium(III) and of the Infinite RMX_3 Linear Chain Complexes
American Chemical Society Symposium Series 5, 142-163 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and NSF-31016X

D. S. Simons, B. N. Colby, and C. A. Evans, Jr.
Electrohydrodynamic Ionization Mass Spectrometry - The Ionization of Liquid Glycerol and Non-Volatile Organic Solutes
Journal of Mass Spectrometry and Ion Physics 15, 291-302 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

S. C. Sorenson, J. A. Wronkiewicz, L. B. Sis, and G. P. Wirtz
Properties of $LaCoO_3$ as a Catalyst in Engine Exhaust Gases
Bulletin of the American Ceramic Society 53, 446-449 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026 and by the Advanced Research Projects Agency under Contract SC-131

V. E. Van Doren and A. Barry Kunz
Approximate Calculation of the Electronic Structure of Solid Surfaces and Interfaces Between Material Media
Physical Review 10, 3578-3583 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026 and by the Aerospace Research Lab under Contract F-33615-72-C-1506

H. Yasuda, M. Walczak, W. Rhine and G. Stucky
The Oxidation Reactions of Organolithium-N,N,N',N'-tetramethylethylenediamine Complexes
Journal of Organometallic Chemistry 90, 123-128 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

R. Zerger, W. Rhine and G. D. Stucky
π Groups in Ion Pair Bonding. The Effect of the Cation on the Structural and Spectroscopic Properties of Fluorenyl Ion Pairs
Journal of the American Chemical Society 96, 5441-5448 (1974)
Supported by the National Science Foundation under Grant DMR-72-03026

Richard Zerger, Wendell Rhine and Galen Stucky
The Sterochemistry of Polynuclear Compounds of the Main Group Elements, The Bonding and the Effect of Metal Hydrogen Carbon Interactions in the Organolithium Compounds
Journal of the American Chemical Society 96, 6048-6055 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GP-31016

Richard Zerger and Galen Stucky
Unsaturated Organometallic Compound of the Main Group Elements. Dicyclopentadienylcalcium
Journal of Organometallic Chemistry 80, 7-17 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GP-31016

5. Mechanical Properties of Materials

G. P. Asselin and C. M. Wayman
Nucleation and Growth on Tungsten Films Evaporated on NaCl
Physica Status Solidi (a) 24, 675-690 (1974)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

D. G. Chakrapani and E. N. Pugh
The Transgranular SCC of a Mg-Al Alloy:
Crystallographic, Fractographic and Acoustic-Emission Studies
Metallurgical Transaction 6A, 1155-1163 (1975)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

H. Y. Chang, R. K. Viswanadham and C. A. Wert
Age Hardening in the V-C and Nb-C Systems
Metallurgical Transaction 5, 1907-1917(1974)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

H. Y. Chang and C. A. Wert
Precipitation of Carbides in Deformed Vanadium
Metallurgical Transaction 5, 1671-1676 (1974)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

T. P. Darby and C. M. Wayman
Anomalous Diffraction Doublet from Gold Films on Graphite Substrates
Philosophical Magazine 30, 1171-1175 (1974)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

T. P. Darby and C. M. Wayman
Growth of Gold Films on Air- and Vacuum-Cleaved Molybdenite
Physica Status Solid (a) 25, 585-590 (1974)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

T. P. Darby and C. M. Wayman
Nucleation and Growth of Gold Films on Graphite I:
Effects of Substrate Condition and Evaporation Rate
Journal of Crystal Growth 28, 41-52 (1975)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

Hamish L. Fraser and Ian P. Jones
A Note on the Increase in Usable Foil Thickness in Scanning Transmission
Electron Microscopy
Philosophical Magazine 31, 225-228 (1975)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

E. R. Fuller, Jr. and W. F. Weston
Relation Between Elastic-Constant Tensors of Hexagonal and Cubic Structures
Journal of Applied Physics 45, 3773-3776 (1974)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

E. R. Fuller, Jr., A. V. Granato, J. Holder, and E. R. Naimon
Ultrasonic Studies of the Properties of Solids
Solid State Volume of Methods of Experimental Physics, edited by
R. V. Coleman (Academic Press, 1974), Vol. II., p. 371
Supported by the Advanced Research Projects Agency under Contract
DAHC-15-73-G10, by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198, and by the National Science Foundation

J. A. Garber and A. V. Granato
Fourth-Order Elastic Constants and the Temperature Dependence of
Second-Order Elastic Constants in Cubic Materials
Physical Review B11, 3998-4007 (1975)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

J. A. Garber and A. V. Granato
Theory of the Temperature Dependence of Second-Order Elastic Constants
in Cubic Materials
Physical Review B11, 3990-3997 (1975)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

J. Holder, A. V. Granato and L. E. Rehn
Effects of Interstitials and Close Pairs on the Elastic Constants
of Copper
Physical Review B10, 363-375 (1974)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198 and the National Science Foundation under
Grant DMR-72-03026

J. Holder, A. V. Granato, and L. E. Rehn
Experimental Evidence for Split Interstitials in Copper
Physical Review Letters 32, 1054-1057 (1974)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

G. Matusiewicz, R. Booker, J. Keiser and H. K. Birnbaum
On Gorsky Measurements of Hydrogen Diffusion in Niobium
Scripta Metallurgy 8, 1419-1426 (1974)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

L. E. Rehn, J. Holder, A. V. Granato, R. R. Coltman and F. W. Young, Jr.
Effects of Thermal Neutron Irradiation on the Elastic Constants of Copper
Physical Review B10, 349-362 (1974)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198 and the National Science Foundation under
Grant DMR-72-03026

H. C. Tong and C. M. Wayman
Thermodynamics of Thermoelastic Martensitic Transformations
Acta Metallurgica 23, 209-215 (1975)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198 and by the Army Research Office (Durham)

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)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198 and by the National Science Foundation

H. C. Tong and C. M. Wayman
Characteristic Temperatures and Other Properties of Thermoelastic Martensites
Acta Metallurgica 22, 887-896 (1974)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198 and by the National Science Foundation

H. C. Tong and C. M. Wayman
Direct Evidence of Pretransformation Lattice Instabilities
Physical Review Letters 32, 1185-1188 (1974)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

H. C. Tong and C. M. Wayman
A Simplified Calorimeter for Determining Latent Heats of
Martensitic Transformations at Low Temperatures
Metallurgica Transactions 5, 1445 (1974)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198 and by the Army Research Office (Durham)

C. M. Wayman
Shear Transformations and Microstructure
Metallography 8, 105-130 (1975)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198 and by the Army Research Office (Durham)

C. M. Wayman and T. P. Darby
Nucleation and Growth of Gold Films on Graphite II:
The Effect of Substrate Temperature
Journal of Crystal Growth 28, 53-67 (1975)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

Wendell S. Williams and Lance Breger
Analysis of Stress Distribution and Piezoelectric Response in Cantilever
Bending of Bone and Tendon
Annals of the New York Academy of Science 238, 121-130 (1974)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

J. Zahavi and M. Metzger
Breakdown of Films and Initiation of Pits on Aluminum During Anodizing
Localized Corrosion, NACE-3, 547-555 (1974)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

Nestor J. Zaluzec and Hamish L. Fraser
The Origin of Dislocation with $\underline{b}$ = <110> in Single Crystals of β-NiAl
Compressed Along <001> at Elevated Temperatures
Scripta Metallurgical 8, 1049-1054 (1974)
Supported by the U. S. Energy Research and Development Administration
under Contract AT(11-1)-1198

6. Semiconductor Materials and Devices

J. C. Campbell, N. Holonyak, Jr., M. G. Craford, and D. L. Keune
Band Structure Enhancement and Optimization of Radiative Recombination in $GaAs_{1-x}P_x$:N (and $In_{1-x}Ga_xP$:N)
Journal of Applied Physics 45, 4543-4553 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation under Grant GH-33771

J. C. Campbell, N. Holonyak, Jr., A. B. Kunz, and M. G. Craford
Effect of Crystal Composition on "Quasi-Direct" Recombination and LED Performance in the Indirect Region of $GaAs_{1-x}P_x$:N
Applied Physics Letters 25, 44-47 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-33771, by the Advanced Research Projects Agency under Contract HC-15-73-G10, and by the Aerospace Reserach Lab under Contract F-33615-72-C-1506

J. C. Campbell, N. Holonyak, Jr., A. B. Kunz, and M. G. Craford
Model Calculations for Radiative Recombination in Zn-N-Doped $GaAs_{1-x}P_x$ in the Direct and Indirect Composition Region
Physical Review B 9, 4314-4322 (1974)
Supported by the National Science Foundation under Grants DMR-72-03026 and GH-33771, by the Advanced Research Projects Agency under Contract HC-15-73-G10, and by the Aerospace Research Lab under Contract F-33615-72-C-1506

J. C. Campbell, N. Holonyak, Jr., M. H. Lee, and A. B. Kunz
Recombination Processes Involving Zn and N in $GaAs_{1-x}P_x$
Physical Review B 10, 1755-1757 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the National Science Foundation under Grants DMR-72-03026 and GH-33771, and by the Aerospace Research Lab under Contract F-33615-72-C-1506

J. J. Coleman, W. R. Hitchens, N. Holonyak, Jr., M. J. Ludowise, J. O. Groves, and D. L. Keune
Liquid Phase Epitaxial $In_{1-x}Ga_xP_{1-z}As_z/GaAs_{1-y}P_y$ Quaternary (LPE)-Ternary (VPE) Heterojunction Lasers ($x\sim0.70$, $z\sim0.01$, $y\sim0.40$; $\lambda<6300$ Å, 77°K)
Journal of Applied Physics Letters 25, 725-727 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation under Grant DMR-72-03045-A01

J. J. Coleman, N. Holonyak, Jr., A. B. Kunz, W. O. Groves, D. L. Keune, and M. G. Craford
Resonant Enhancement (?) of the Recombination Probability at the Nitrogen-Tray, Γ-Band Edge Crossover in $GaAs_{1-x}P_x$:N($E_N=E_\Gamma, x=x_N$)
Solid State Communications 16, 319-322 (1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the National Science Foundation under Grants DMR-72-03026 and DMR-72-03046-A01, and by the Aerospace Research Lab under Contract F-33615-72-C-1506

J. J. Coleman, N. Holonyak, Jr., M. J. Ludowise, A. B. Kunz, M. Altarelli, W. O. Groves, and D. L. Keune
Index Dispersion Above the Fundamental Band Edge in Nitrogen-Doped $GaAs_{1-y}P_y$ ($y=0.38m$ $E_N>E_\Gamma$)
Physical Review Letters 33, 1566-1569 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the National Science Foundation under Grants DMR-72-03026 and DMR-72-03045-A01, and by the Aerospace Research Lab under Contract F-33615-72-C-1506

J. J. Coleman, N. Holonyak, Jr., M. J. Ludowise, P. D. Wright, W. O. Groves, and D. L. Keune
Liquid Phase Epitaxial $In_{1-x}Ga_xP_{1-z}As_z/GaAs_{1-y}P_y$ Heterojunction Lasers
IEEE Journal of Quantum Electronics QE-11, (1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation under Grant DMR-72-03045-A01

J. J. Coleman, N. Holonyak, Jr., M. J. Ludowise, P. D. Wright, W. O. Groves, D. L. Keune, and M. G. Craford
Heterojunction Laser Operations of N-Free and N-Doped $GaAs_{1-t}P_y$ ($y=0.42$-0.43, $\lambda\sim6200$ Å, 77°K) Near the Direct-Indirect Transition ($y\sim y_c\simeq0.46$)
Journal of Applied Physics 46, (1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation under Grant DMR-72-03045-A01

M. G. Craford and N. Holonyak, Jr.
The Optical Properties of the Nitrogen Isoelectronic Trap in $GaAs_{1-x}P_x$
Optical Properties of Solids: New Developments, edited by B. O. Seraphin (North-Holland Publishing Co., Amsterdam, 1975), Chapter 5
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

Karl Hess, Arnost Neugroschel, C. C. Shiue, and C. T. Sah
Nonohmic Electron Conduction in Silicon Surface Inversion Layers at Low Temperatures
Journal of Applied Physics 46, 1721-1727 (1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the Air Force Office of Scientific Research under Contract AFOSR-71-2067, and by the National Science Foundation under Grant GK-30283

W. R. Hitchens, N. Holonyak, Jr., M. H. Lee, and J. C. Campbell
Liquid Phase Epitaxial Growth and Photoluminescence Characterization of Laser-Quality (100) $In_{1-x}Ga_xP$
Journal of Crystal Growth 27, 154-165 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

W. R. Hitchens, N. Holonyak, Jr., M. H. Lee, and J. C. Campbell
$In_{1-x}Ga_xP$ ($x \simeq 0.63$) Yellow Injection Laser (λ = 5900 Å, 77°K) Grown by the Method of Liquid Phase Epitaxy
Phys. Tekh. Poluprovo. 8, 2418-2424 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

W. R. Hitchens, N. Holonyak, Jr., M. H. Lee, J. C. Campbell, J. J. Coleman, W. O. Groves, and D. L. Keune
Liquid Phase Epitaxial (LPE) Grown-Junction $In_{1-x}Ga_xP$(x~0.63) Laser of Wavelength λ~5900 Å (2.10 eV, 77°K)
Applied Physics Letters 25, 352-354 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the National Science Foundation under Grant GH-33771, and by the U. S. Army Night Vision Laboratory under Contract DAAK-02-72-C-0076

M. H. Lee, N. Holonyak, Jr., W. R. Hitchens, J. C. Campbell, and M. Altarelli
The Direct-Indirect Transition in $In_{1-x}Ga_xP$
Solid State Communications 15, 981-985 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the National Science Foundation under Grant GH-33771, by the U. S. Army Night Vision Laboratory under Contract DAAK-02-72-C-0076, and by the Army Research Office under Contract DAHC-04-74-C-0005

M. H. Lee, N. Holonyak, Jr., R. J. Nelson, D. L. Keune, and W. O. Groves
Lifetime Spectra (77°K) of Nitrogen-Doped $GaAs_{1-x}P_x$
Journal of Applied Physic 46, 1290-1298 (1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation under Grant DMR-72-030450A01

M. H. Lee, N. Holonyak, Jr., R. J. Nelson, D. L. Keune, and W. O. Groves
Behavior of Carrier Lifetime Spectra (77°K) in $GaAs_{1-x}P_x$
Journal of Applied Physics 46, 323-331 (1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation under Grant GH-33771

M. J. McNutt and C. T. Sah
The Effects of Spatially Inhomogeneous Oxide Charge Distribution on the MOS Capacitance-Voltage Characteristics
Journal of Applied Physics 45, 3916-3921 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the Air Force Office of Scientific Research under Contract AFOSR-71-2067, and by the National Science Foundation under Grant GK-30283

M. J. McNutt and C. T. Sah
Experimental Observations of the Effects of Oxide Charge Inhomogeneity on Fast Surface State Density from High Frequency MOS Capacitance-Voltage Characteristics
Journal of Applied Physics Letters 26, 378-380 (1975)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the Air Force Office of Scientific Research, and by the National Science Foundation under Grant GH-33634

Sokrates T. Pantelides and C. T. Sah
Theory of Localized States in Semiconductors I: New Results Using an Old Method
Physical Review B 10, 621-637 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the Air Force Office of Scientific Research, and by the National Science Foundation under Grant GH-33634

Sokrates T. Pantelides and C. T. Sah
Theory of Localized States in Semiconductors II: The Pseudo Impurity Theory Application to Shallow and Deep Donors in Silicon
Physical Review B 10, 638-658 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the Air Force Cambridge Research Lab under Contract F-19628-72-C-0199

C. T. Sah, C. T. Wang, and S. H. Lee
Junction Edge Region Thermally Stimulated Capacitance (SCAP) of n-Si Doped with Phosphorus and Bismuth
Applied Physics Letters 25, 523-524 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the Air Force Cambridge Research Lab under Contract F-19628-72-C-0199

V. A. Voronin, W. D. Stewart, Jr., G. W. Marshall, J. B. Wagner, Jr., H. M. Macksey, and N. Holonyak, Jr.
A Scanning Electron Microscope Study of $In_{1-x}Ga_xP$
Journal of the Electrochemical Society 121, 1657-1661 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation under Grants GH-33634 and GH-33771

PH.D. DISSERTATIONS

July 1, 1974 - June 30, 1975

Charles Henry Aldrich, III (D. Pines, Adviser), "Polarization Potentials and Elementary Excitations in Strongly Interacting Quantum Liquids," October 1974. Supported by the National Science Foundation under Grant DMR-72-03026 and by the Army Research Office under Contract DAHC-04-74C-005.

David William Allender (J. Bardeen, Adviser), "Model for an Exciton Mechanism of Superconductivity in Planar Geometry," January 1975. Supported by the National Science Foundation under Grant DMR-72-03026 and by the Army Research Office under Contract DA-HC04-74-005.

Joseph Gary Baldoni II (W. S. Williams, Adviser), "High Temperature Deformation Behavior of Cemented Carbide Cutting Tools," January 1975. Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198.

Robert Charles Birtcher (J. S. Koehler, Adviser), "The Recovery of Lead After Electron Irradiation at 1.5 K," May 1975. Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198.

Marshall Allen Bowen (J. D. Dow, Adviser), "Topics in the Theory of Condensed Matter: Diffusion Thermoelectric Power in the Alkali Metals and Electroabsorption by Acoustoelectric Domains," January 1975. Supported by the National Science Foundation under Grant DMR-72-03026.

James William Bray (J. Bardeen, Adviser), "Fluctuation Conductivity from Charge Density Waves in Pseudo-One-Dimensional Systems," October 1974. Supported by the National Science Foundation under Grant GH-33634 and by the Advanced Research Projects Agency under Contract SD-131.

Lance Harris Breger (W. S. Williams, Adviser), "Piezoelectric Response of Bone and Tendon Subjected to Inhomogeneous Stress," October 1974. Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198.

John H. Campbell (J. Jonas, Adviser), "Raman and NMR Studies of the Effects of Density and Temperature on the Molecular Dynamics in Fluids," January 1975. Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation under Grant GP-28268X.

D. G. Chakrapani (E. N. Pugh, Adviser), "Transgranular Stress-Corrosion Cracking of a Magnesium-Aluminum Alloy," May 1975. Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198.

S. Chakravorty (C. M. Wayman, Adviser), "Crystallography of the Thermoelastic Martensitic Transformation in Ni-Al Alloys," May 1975. Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198.

Jim E. Clemans (M. V. Klein, Adviser), "Low Temperature Thermal Conductivity Measurements on Solid Neon at Constant Volume," January 1975. Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation under Grants DMR-72-03026 and GH-37757.

Thomas P. Darby (C. M. Wayman, Adviser), "Nucleation and Growth of Gold Thin Films Vapor Deposited on Single Crystal Graphite Substrates," May 1974 (omitted from last years report). Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198.

Dan L. Fanselow (H. G. Drickamer, Adviser), "The Effect of High Pressure on a Series of Photochromic, Thermochromic, and Piezochromic Bianthrones," October 1974. Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198.

James Terwillegar Folinsbee (A. C. Anderson, Adviser), "The Kapitza Resistance at Metal-Helium Interfaces," October 1974. Supported by the National Science Foundation under Grant DMR-72-03026.

David Martin Follstaedt (C. P. Slichter, Adviser), "A Nuclear Magnetic Resonance Study of Dilute Copper-Vanadium Alloys," January 1975. Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198.

T. D. Gierke (W. H. Flygare, Adviser), "Depolarized Rayleigh Light Scattering Studies of Orientational Pair Correlations in a Nematic Liquid Crystal. The Coupled Translational-Rotational Diffusion of Rod-Like Macromolecules and the Method of Atom Dipoles," October 1974. Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10.

S. L. Hartford (W. H. Flygare, Adviser), "Quasielastic Rayleigh Laser Light Scattering from Macromolecules, Electrophoretic Light Scattering, and the Molecular Zeeman Effect and Deuterium Coupling Constant in Methinophosphide," May 1975. Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation.

Richard Spencer Hockett (D. Lazarus, Adviser), "Search for Magneto-Flicker Noise in Potassium," October 1974. Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198.

James N. Humenik (G. P. Wirtz and R. L. Cook, Advisers), "Reactions Between Molybdenum Disilicide and Vanadium Oxides at Elevated Temperatures," January 1975. Supported by the National Science Foundation under Grant DMR-72-03026.

Patrick S. Ireland (T. L. Brown, Adviser), "Pulse and Double Resonance Methods in Nuclear Quadrupole Resonance Spectroscopy," May 1975. Supported by the National Science Foundation under Grant DMR-72-03026.

Jared Logan Johnson (J. Bardeen, Adviser), "Current Flow in Inhomogeneous Superconductors," October 1974. Supported by the Advanced Research Projects Agency, by the Army Research Office, and by a National Science Foundation Traineeship.

Harold Richard Kerchner (D. M. Ginsberg, Adviser), "The Superconducting Penetration Depth in Thin Films of Lead," October 1974. Supported by the National Science Foundation under Grant DMR-72-03026.

Hosakere Ananda Kumar (C. G. Bergeron, Adviser), "The Effect of Impurities on the Crystal Growth of Lead Tetraborate from its Melt," October 1974. Supported by the National Science Foundation under Grant DMR-72-03026, by the Advanced Research Projects Agency under Contract HC-15-67-C-2110, by the Owens-Corning-Fibre Glass Fellowship, and by a University of Illinois Fellowship.

Philippe Lecocq (C. A. Wert, Adviser), "The Solubility of Hydrogen in Tantalum," October 1974. Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198.

Michael H. Lee (N. Holonyak, Jr., Adviser), "Lifetime Spectra of Gallium Arsenide Phosphide and Nitrogen-Doped Gallium Arsenide Phosphide," October 1974. Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the National Science Foundation under Grants GH-33634 and GH-33771, by the U. S. Army Night Vision Laboratory under Contract DAAK-02-72-C-0076, and by the University Industrial Affiliates Program.

Michael John McNutt (C. T. Sah, Adviser), "Theory and Experiments on High Frequency Metal-Oxide-Semiconductor Capacitance," October 1974. Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10.

Arlene McPherson (G. D. Stucky, Adviser), "Structural Studies of Low Valent Titanium Organometallic and Unsaturated Organoaluminum Compounds," January 1975. Supported by the National Science Foundation under Grant DMR-72-03026 and by the Advanced Research Projects Agency.

Joan Laverne Mitchell (D. Lazarus, Adviser), "Effect of Heterovalent Impurities Co-Diffusing with Monovalent Tracers in Ionic Crystals," October 1974. Supported by the U. S. Energy and Research Development Administration under Contract AT(11-1)-1198.

B. Y. Okamoto (H. G. Drickamer, Adviser), "The Effects of High Pressure on the Electronic Structure of Some Purines, Pyrimidines and Aromatic Hydrocarbons," October 1974. Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198.

Hugh J. Parkhurst, Jr. (J. Jonas, Adviser), "High Pressure Nuclear Magnetic Resonance Studies of Self-Diffusion in Liquids," October 1974. Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, and by the National Science Foundation under Grants DMR-72-03026 and GP-28268X.

Daniel James Phelps (C. P. Flynn, Adviser), "Optical and Electrical Studies of Alkali Metal-Rare Gas Alloys," October 1974. Supported by the National Science Foundation under Grant DMR-72-03026 and by the Advanced Research Projects Agency under Contract HC-15-67-C-0221.

Sherrill Austin Puckett (D. Y. Curtin and I. C. Paul, Advisers), "Recent Studies in Solid State Organic Chemistry," May 1975. Supported by the National Science Foundation under Grant DMR-72-03026.

David Thomas Read (A. V. Granato, Adviser), "Bias Stress Detection of Dislocation Resonance in Lead," May 1975. Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198.

Gregory Jude Sellers (A. C. Anderson, Adviser), "Low Temperature Anomalies in Niobium, Vanadium and Tantalum," October 1974. Supported by the National Science Foundation under Grant DMR-72-03026 and by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198.

Vishwa Nath Shukla (G. Wirtz, Adviser), "Electronic Conduction in Thallic Oxide," October 1974. Supported by the National Science Foundation under Grant DMR-72-03026 and by the Advanced Research Projects Agency under Contract HC-15-67-C-0221.

Darryl L. Smith (J. D. Dow, Adviser), "Studies of the Theory in Solids," October 1974. Supported by the National Science Foundation under Grant DMR-72-03026 and by the Advanced Research Projects Agency under Contract HC-15-67-C-0221.

Thomas S. Stakelon (C. P. Slichter, Adviser), "Nuclear Magnetic Resonance in Single Crystals of the Magnetic Alloys: CuFe, CuCo, and CuNi," October 1974. Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198.

Richard Alonzo Tilton, II (C. P. Flynn, Adviser), "Optical Studies of Rare Gas Impurities in Alkali Metals," October 1974. Supported by the National Science Foundation under Grant DMR-72-03026 and by the Advanced Research Projects Agency under Contract HC-15-67-C-0221.

Michael Walczak (G. D. Stucky, Adviser), "Structure, Bonding and Reactivity Studies of Unsaturated Organolithium Compounds," January 1975. Supported by the National Science Foundation under Grant DMR-72-03026 and by the Advanced Research Projects Agency.

John Raymond Wallace (D.F.S. Natusch, Adviser), "The Chemical and Physical Characterization of Airborne Particulate Matter," October 1974. Supported by the National Science Foundation under Grants DMR-72-03026, GP-33273, GP-42330X, GI-31605, and by the E. I. du Pont Company.

Richard John Wallat (J. Holder, Adviser), "The Phase Transition of the Rubidium Halides," May 1975. Supported by the National Science Foundation under Grant DMR-72-03026.

John Shi Sun Wei (F. C. Brown, Adviser), "Polaron Transport in Silver Bromide," May 1974. Supported by the National Science Foundation under Grant DMR-72-03026, and by the U. S. Army Research Office (Durham) under Contract ARO-D31-124-73-G103. (Omission from last year's report).

David J. Wilbur (J. Jonas, Adviser), "Fourier Transform NMR in Liquids at High Pressure," October 1974. Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10.

M.S. THESES

July 1, 1974 - June 30, 1975

(This list does not include M.S. degrees for which written theses were not required.)

Yue-Kong Au (C. M. Wayman, Adviser), "Some Electrical Properties of Amorphous Germanium, Indium Antimonide and Gallium Antimonide Films," August 1974. Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198.

Peter S. Bachert (M. M. McNutt, Adviser), "High-Frequency Capacitance-Voltage Analysis of MOS Surface States," January 1975. Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the Air Force Office of Scientific Research under Grant AFOSR-71-2067, and by the National Science Foundation under Grant GK-30283.

M. Cassidy (C. M. Wayman, Adviser), "An Electron Microscopy Study of the Substructure of β-Hydride in Vanadium," May 1975. Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198.

Howard Gabel (E. N. Pugh, Adviser), "An Electron Microprobe Study of the Composition of Tarnish Films on Copper-Zinc, Copper-Aluminum and Copper-Nickel Alloys," January 1974 (omitted from last year's report). Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198 and by the Army Research Office (Durham).

E. N. Hockert (H. G. Drickamer, Adviser), "The Effect of Pressure on the Electronic Spectra of Some Salicylidine Anilines," May 1975. Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198.

G. L. House (H. G. Drickamer, Adviser), "Effects of High Pressure on the Luminescence of Zinc Sulfide Phosphors," May 1975. Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198.

Charles John Leedecke (C. G. Bergeron, Adviser), "The Crystallization of Potassium Octaborate from its Pure Stoichiometric Melt," October 1974. Supported by the National Science Foundation under Grant DMR-72-03026 and by the Pittsburgh Plate Glass Industries Fellowship.

Daniel Sutherland Petty (W. S. Williams, Adviser), "Investigation of Preferential Etch Patterns Created in Human Dental Enamel During Acid Attack," October 1974. Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198.

C. E. Tyner (H. G. Drickamer, Adviser), "Effects of Pressure on Oxygen Dominated Phosphors," May 1975. Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198.

T. Wilkin (C. A. Wert, Adviser), "The Morphological Structures Produced During Reduction of Blue Tungsten Oxide to Tungsten Metal," May 1975. Supported by the U. S. Energy Research and Development Administration under Contract AT(11-1)-1198.

Phillip Douglas Wright (N. Holonyak, Jr., Adviser), "Spectral Properties of Gallium Arsenide Phosphide Single Heterojunction Lasers," May 1975. Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the National Science Foundation under Grant DMR-72-03045-A01, and by the University Industrial Affiliates Program.

ADDITIONAL PROJECTS IN MATERIALS SCIENCE

AT THE UNIVERSITY OF ILLINOIS

C. J. Altstetter, Professor of Physical Metallurgy
Hydrogen Embrittlement in the Iron-Nickel-Chromium System
National Science Foundation Grant NSF-DMR74-24648
Phase Instability During Low-Cycle Fatigue of Steel
U. S. Army Research Office (Durham) Contract DA-ARO-D-31-124-73-G43

A. C. Anderson, Professor of Physics
A Low Temperature Investigation of Amorphous Dielectrics
National Science Foundation Grant NSF-DMR75-09566

J. Bardeen, Professor of Physics
Theoretical Problems in Solid State and Low Temperature Physics
U. S. Army Research Office (Durham) Contract DAHC-04-74-C-0005

G. Baym, C. J. Pethick and M. Wortis, Professors of Physics
Properties of Solids and Many Particle Systems
National Science Foundation Grant NSF-GP-40395

P. A. Beck, Professor of Physical Metallurgy
Alloys of Transition Metals
National Science Foundation Grant NSF-GH-37568X1

H. K. Birnbaum, Professor of Physical Metallurgy
An Investigation of the Mechanisms of Hydrogen Embrittlement in B.C.C. Metals
U. S. Office of Naval Research Contract ONR-N0014-75-C-1012

T. L. Brown, Professor of Chemistry
Organometallic Chemistry
National Science Foundation Grant NSF-MPS71-03201

D. Y. Curtin, Professor of Chemistry
Solid State Organic Chemistry
National Science Foundation Grant NSF-GP-34545X2

J. D. Dow, Professor of Physics
Theory of Solids and Polyatomic Systems
National Science Foundation Grant NSF-GH-39132

G. Ehrlich, Professor of Physical Metallurgy
Semiconductor Surface Chemistry
U. S. Air Force Office of Scientific Research Contract AF-OSR-72-2210C
Decomposition of Hydrocarbons
National Science Foundation Grant NSF-DMR72-02937
Atomic Exploration of Crystal Surfaces
National Science Foundation Grant NSF-DMR74-23811

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Ion Microprobe Mass Spectrometry
National Science Foundation Grant NSF-MPS74-05745
Mass Spectrometry of Nonvolatile, Organic Compounds
National Institute of Health Contract GM-19749

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High Resolution Microwave Spectroscopy
National Science Foundation Grant MPS 73-04556

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Electronic Structure of Hydrogen in Metals and on Metal Surfaces
U.S. Office of Naval Research Contract ONR-N00014-75-C-0918

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The Effects of Oxidation on the Physical and Mechanical Properties of Intermetallic Compounds
National Science Foundation Grant ENG-74-17512

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Morphological Changes in Oriented Polymer Crystallization
National Science Foundation Grant DMR-75-10284

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Properties of Superconductors
National Science Foundation Grant DMR-73-07581

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Defect Interactions in Crystals
National Science Foundation Grant DMR-75-14726

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Sputtered Coatings on Metal
National Science Foundation Grant GH-44310
Sputtered Deposition
National Science Foundation Grant GH-32651

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Research on Semiconductors Luminescence and Lasers
National Science Foundation Grant DMR-72-03045

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Nuclear Magnetic Resonance Study of Relaxation Phenomena
National Science Foundation Grant MPS-74-19428
High Pressure Nuclear Magnetic Resonance Relaxation Study of Supercritical Dense Fluids
Air Force Office of Scientific Research Contract AFOSR 72-2286

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Raman Scattering from Electronic Excitations in Semiconductors
National Science Foundation Grant DMR-73-07564

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Electronic Structure of Solid Surfaces and Interfaces
Air Force Office of Scientific Research Contract AFOSR-AF-F-33615-72-C-1506

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Physical Theories of Liquid Crystals
National Science Foundation

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A Study in Very Thin Superfluid Helium Films in Quartz Capsules
National Science Foundation Grant DMR-72-03291

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Interactions of Toxic Metal Species with Biomolecules
Health, Education and Welfare Grant 5R01ES00997-02

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Liquid Phase Sintering of Diphasic Dielectric Ceramic Mixtures
National Science Foundation Grant DMR-75-10327

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Astrophysical Applications of Microscopic Many-Body Theory
National Science Foundation Grant MPS-75-08790

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The Mechanism of Stress-Corrosion Cracking
Army Research Office (Durham) ARO-DA-HC-04-74-G-0127

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Circuit Models of Semiconductor Devices
National Science Foundation Grant GK-30283
Interface and Bulk Phenomena in Solid State Components
Useful in Air Force Systems
Air Force Office of Scientific Research Contract AF-OSR-71-2067

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Comparative Critical Point Measurements
National Science Foundation Grant DMR-71-01797

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Studies of Superconductivity in Metal-Hydrogen Systems
National Science Foundation Grant DMR-75-13083

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An Experimental Investigation of Spin-Lattice Relaxation Rates
and Ligand Bonding of Octahedrally Coordinated Rare Earth Ions
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Main Group and Transition Metal Organometallic Compounds
National Science Foundation Grant MPS-74-23000

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Martensitic Transformations in Iron Alloys
Army Research Office (Durham) Contract ARO-DA-HC-04-74-G-0134
Properties and Characteristics of Shape Memory ('Marmen') Materials
National Science Foundation Grant DMR-74-23684

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Electronic and Mechanical Effects of Hydrogen on the Elastic Compounds of VB Elements
National Science Foundation Grant DMR-73-02581


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