PURDUE UNIVERSITY

TWELFTH PROGRESS REPORT
October 1, 1972 — September 30, 1973

on
MATERIALS SCIENCES RESEARCH
(Supporting agencies listed on inside cover)

submitted to the
DIVISION OF MATERIALS RESEARCH
of the
NATIONAL SCIENCE FOUNDATION (GH 33574 and GH 33574 A1)
by the
MATERIALS SCIENCES COUNCIL

November 30, 1973
Advanced Research Projects Agency
American Society of Heating, Refrigerating, and Air Conditioning Engineers
Atomic Energy Commission
Basil S. Turner Foundation
Defense Supply Agency
Delco Electronics
Inland Steel - Ryerson Foundation
Lawrence Livermore Laboratory
National Aeronautic and Space Administration
National Science Foundation
Office of Naval Research
Office of Standard Reference Data
National Bureau of Standards
Office of Water Resources Research
Polish Academy of Sciences
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United States Air Force Office of Scientific Research
United States Air Force Rome Air Development Center
United States Air Force Systems Command
United States Air Force Weapons Laboratory
United States Army Electronics Command
United States Army Research Office - Durham
United States Navy
Western Electric Company

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INTRODUCTION

The research described in this report was performed during the period October 1, 1972 through September 30, 1973 in the area of materials science under sponsorship of agencies listed on the inside cover and cited at the end of each item of technical information. A considerable fraction of the work was carried out as part of the MRL program of the Division of Materials Research of NSF (GH 33574) and of the materials research sponsored by the Materials Sciences Office of ARPA. Both of these programs were administered by the Materials Sciences Council. Participants in these programs include faculty and research associates in the Departments of Physics, Chemistry, and Geosciences, and in the Schools of Materials Engineering, Electrical Engineering, Mechanical Engineering, Aeronautics and Astronautics, Civil Engineering, Chemical Engineering, and at the Thermophysical Properties Research Center.

A large number of central facilities which became operational last year are continuing to contribute to materials research. In addition, the Council initiated partial support of the X-Ray Photoelectron Spectroscopy (ESCA) Facility; the X-Ray and Crystal Growth Facilities have also been further upgraded. A brief summary of available facilities is provided below.

There is a continuing trend towards more collaborative research among senior investigators from different disciplines, as is evident by perusal of the Index of Contributions. A very large fraction of the materials research in the MRL program can readily be grouped in the following categories of cluster areas: (1) acousto-optic, acousto-electric, and ultrasonic research; (2) research for elucidating transport phenomena in
well characterized oxides; (3) frontier research in semiconductors and semiconductor devices; (4) modern approaches to the study of interfaces and interfacial phenomena; and (5) materials sciences research relevant to natural resources. These are briefly described in a separate section.

The short descriptions of the individual research programs in the main body of the report are listed alphabetically by the name of the principal investigator. Such descriptions also contain a listing of all personnel involved in the research, of resulting publications, and of associated meeting speeches. A combined publications list is provided in Appendix A and a listing of M.S. and Ph.D. theses resulting from the research is assembled in Appendix B. A name index of individuals whose research is reported below is included in Appendix C.

Description of Central Facilities

1. The Central Facilities listed below, supported wholly or in part by the MRL program, are presently available for use by researchers in materials science at Purdue.

The Central Materials Preparation Facility (Professor J. M. Honig in charge)

This operation is managed on a day-to-day basis by a part-time research associate in consultation with the professor-in-charge. These individuals are responsible for the setting of policies and for overall administration, including the establishment of priorities for service; they are also expected to provide scientific advice on any problems arising in crystal growth and to investigate and recommend procedures for growth of new types of crystals for which there is a demand. The actual crystal growth is carried out by the research associate in charge, by a second full-time research associate, and by a technician, supported by the Council.

The equipment consists of several units for crystal growth by the Bridgman Technique, by multi-zone furnaces, by r.f. coupling, by resistance heating of crucibles, and by arc melting techniques. In the latter
two cases the Czochralski-Kyropoulos method of pulling single crystals from the melt is employed. Equipment for zone purification and zone leveling, and for cutting of samples from boules is also in service. A program for duplicating major pieces of equipment is in progress; this will provide graduate students with an opportunity to grow their own crystals under close supervision, particularly in research projects where there exists a need for a continuing supply of such crystals. The facility provides the needed chemicals and supplies the crystals to the users without charge.

At present the types of crystal grown include elemental, III-V, and II-VI compound semiconductors, metal oxides, alkali metal and alkaline earth halides, and intermetallic alloys; on occasion single crystals of organic compounds or other special materials are grown.

Microstructural Analysis Facility (Professors M. A. Dayananda and G. L. Liedl in charge)

a. Electron Microscope: A thirteen-year-old Siemens 100 KV instrument is available for conventional transmission and replica analyses of structure. Resolution of less than 15 Å is attainable. The equipment is maintained and operated by a technician supported by the Council. Specimen preparation is ordinarily performed by the user.

b. Scanning Electron Microscope: A new Jeolco JSM-U3 instrument capable of 100 Å resolution, with TV display and energy dispersive analysis capability is available for both structural and composition studies. The latter is done by energy-dispersive x-ray spectroscopy with the aid of a computer for data reduction. Emphasis is upon teaching researchers to prepare specimens and upon use of microscope with minimal supervision, rather than on operation as a service facility. This instrument is in continuous heavy demand, which necessitates after-hour and weekend use.

c. Electron Microprobe Analyzer: This eight-year-old item of equipment provides capability for compositional analysis by wavelength-dispersive x-ray spectroscopy, with a beam diameter of approximately
4 microns. Accuracy is, in general, better than for compositional analysis obtained with the scanning electron microscope. Use of the instrument is under the direction of Professor Dayananda, a portion of whose salary derives from Council funds.

d. Image Analysis Discriminator: This equipment provides capability for automated microstructural analysis for up to four phases. Particle size distributions, average chord lengths, volume fractions, etc., can all be obtained by computer. Analyses of both optical and scanning electron microscope images can be made. Use of this equipment is under the direction of Professor R. W. Vest.

e. Ion Micromilling Instrument: This equipment is for the preparation of ultrathin and ultrasmooth specimens of nonconductive materials, which are then scanned by the equipment described above.

f. Optical Microscopy and Metallography: Several standard instruments for routine analyses are available.

Central Analysis Facility (Operated in cooperation with the Battelle Memorial Institute, Columbus, Ohio)

Persons requiring analyses pertaining to sample composition or impurity content may obtain such services under a special arrangement with Battelle Memorial Institute. Participants in the MRL program get in touch with Mr. Ben Paris of Battelle Memorial Institute to arrange for the desired analysis by the appropriate chemical or physical techniques; the results are communicated directly to the requestor. Expenses for this operation ordinarily are charged to the specific project under the direction of the principal investigator.

Ultra Low Temperature Facility (Professor P. H. Keesom in charge)

A dilution refrigerator and a He³ refrigerator are in working condition and used on a routine basis. The He³ refrigerator allows measurements between 0.28 and 4.2K and, if necessary, can be used to go up to 20K.
The dilution refrigerator has reached 0.015K and probably can be pushed to 0.10K by turning off the return of the He$^3$ gas. It will then deplete its He$^3$ supply and will stop operating after one or two hours.

Working space for both refrigerators consists of a cylinder 3 cm in diameter and 20 cm in height. A superconducting magnet is available to produce a magnetic field up to 30 kGauss.

Helium consumption of the two refrigerators is nearly the same. It requires approximately 8 L to cool down the system and allows measurement to be made for 20 hours; refilling requires 4 liters.

**Electron Irradiation Facility** (Professor J. W. MacKay in charge)

Four electron accelerators are available for irradiation services:

a. Two Van de Graaff accelerators with energy variable from 0.1 to 1.0 MeV. Maximum electron beam current 250 microamperes (D.C.).

b. Two microwave linear accelerators, i) energy variable from 0.2 to 1.5 MeV, ii) energy variable from 2.5 to 5.0 MeV. These are pulsed machines (1 microsecond pulses at 120 pulses per second) with a maximum average beam current ~1.0u amp and maximum pulsed beam current ~10m amp. Service work involving these machines can be arranged in consultation with Professor J. W. MacKay. Part-time technician help is being supplied by the MRL program.

**Electron Microprobe Facility** (Professor G. Kullerud in charge)

A second electron microprobe facility has been installed in the Department of Geosciences, consisting of an electron optical column, x-y-z specimen stage, turret light microscope, and column isolation system. The x-ray spectrometer system includes three manual/motorized full focus spherical spectrometers and analyzing crystals, as well as x-ray proportional counters. Several data readout system choices are available, and there is provision for future additions of data processing and other automation features. The electron beam size is continuously adjustable from 0.03 to 500 microns.
This instrument, which is partially supported by Council funds, considerably augments the capabilities of the obsolescent microprobe analyzer listed as (c) in the Microstructural Analysis Facility description, and was purchased in part to update the capability on campus and in anticipation of a large increase in demand by users.

**Thermal Analysis Facility (Professor J. R. Cost in charge)**

A new central facility which is being equipped to measure various thermal properties of materials has been set up as part of the MRL. The first item of equipment for this facility, a differential scanning calorimeter, is now installed and available for use. This unit, a Perkin-Elmer DSC-1, has an operating range from $100^0\text{K}$ to $1000^0\text{K}$, variable heating (or cooling) rates from $0.31^0\text{min.}$ to $320^0\text{min.}$, and a full scale sensitivity down to $10^{-4}$ cal/sec. It is a state-of-the-art instrument, showing marked improvement over its predecessor the DSC-2, particularly in baseline linearity and repeatability as well as in temperature control.

The facility is now located in the Chemical and Metallurgical Engineering Building and is under the direction of Professor J. R. Cost. Frequent users of the facility will be instructed in its operation so that they can operate it autonomously after having demonstrated capability.

**ESCA Facility (Professor J. W. Amy in charge)**

The Purdue ESCA Facility consists of a Hewlett-Packard Model 5950 A photoelectron spectrometer. This instrument is equipped with an aluminum anode x-ray source and utilizes a spherical crystal monochromator to isolate the $K_{\alpha}$ radiation.

Variable temperature capability from about liquid nitrogen temperatures to $400^0\text{C}$ is now available. The instrument also contains a sample treatment chamber in which it is possible to evaporate thin films, Argon-ion etch the surface, or react the samples with various gases in situ. The sample is then directly inserted into the spectrometer through a vacuum lock system.
A number of uses are being made of the technique, including studies of chemical structure, band structure, surface chemistry, chemical composition, measurements of Fermi levels, studies of oxides and catalysts.

The ESCA equipment is located in the Department of Chemistry. This is a self-service facility, with training of staff and students being handled by Professor Amy and Dr. Baitinger. An ESCA users group holds weekly noon meetings, and a short course in the practical aspects of ESCA has been held under sponsorship of the Department of Continuing Education on May 14, 15, and 16, 1973.

X-Ray Facility (Professors R. Colella and G. L. Liedl in charge)

Standard operating equipment in the School of Materials Engineering includes four x-ray diffractometers, fluorescence attachments, back reflection Laue Camera, Precession Camera, Debye-Scherrer Camera, high temperature diffractometer attachment, and data acquisition equipment. Standard operating equipment in the Department of Physics includes x-ray diffractometers, fluorescence diffractometer, back reflection Laue Camera, Precession Camera, Weissenberg Camera, powder cameras, and data acquisition equipment. The present facilities allow studies to be made on single crystals and powders, and permits the following types of service work to be carried out: The orientation of single crystals, the identification and checking of elements and compounds, the determination of the number and amount of phases in materials, the determination of crystal symmetries, the precision measurement of lattice parameters, the qualitative chemical analysis by x-ray fluorescence, and the monitoring of variation of lattice parameters as a function of temperature. Work is performed with the assistance of a technician supported by the Council.

Central Facility for the Production and Recovery of Liquid Helium (Professor W. M. Becker in charge)

A central facility for the production of liquid helium is supported in part by the Materials Sciences Council; a helium recovery system is an
integral feature of the facility. Installation of the cryogenic unit, purchased from Cryogenic Technology, Inc., was completed in March 1972. Service is provided for the University at large, as well as for participants in the MRL program. Costs for production of liquid helium and for operation of the facility are met in part by assessing appropriate charges against individual projects. The Council subsidized the operation through purchase of equipment and of supplies needed in the startup, and is continuing to provide funds for personnel and supplies. The facility is operated with the assistance of a part-time technician; operations commenced in early April, 1972.

Central High Magnetic Field Facility (Professor W.M. Becker in charge)

A large superconducting magnet manufactured by Intermagnetics General Corporation was placed in operation in the fall of 1972. The maximum field achieved is \( \approx 144 \) kilogauss. One axial and four radial ports are provided for optical access. The bore of the solenoid (2 inch diameter) allows insertion of a triple-walled dewar with considerable working space for measurements from liquid helium to above room temperature. Such a triple-walled dewar is now available for experiments with the solenoid.

The superconducting magnet is used by qualified investigators who submit requests for magnet time to a committee which supervises the overall operations. The magnet is serviced and operated by a technician supported by the Council, but the research is carried out by staff members and graduate students who have received operating and safety instructions.

Investigators using the facility share costs of the liquid nitrogen and liquid helium needed to cool down and operate the magnet.

LEED-Auger Spectroscopy Facility (Professor S.J. Hruska in charge)

Equipment in this facility is made available to qualified users who desire qualitative and semi-quantitative information of the surface structure and composition of materials at or above room temperature. Equipment permitting such studies to be carried out at low temperatures is to be added in the future. The desired investigation can be performed in ultrahigh vacuum, in the presence of metal vapor, or of noble and reactive gas ambients. In many cases dynamic or static surface chemical
analyses can be carried out. A 4 grid 120° optical setup and 4 grid glancing incidence collector permit LEED, Auger spectroscopy, and differential work function measurements. Peripheral equipment includes specimen manipulators, regulated power supplies for heating, an ultrahigh vacuum system, and a camera system for pattern documentation.

Proton Scattering Microscope (Professor G. L. Liedl in charge)

A proton scattering microscope, loaned by Edwards High Vacuum, Inc., has been installed in the Physics Building as a part of the Central Crystal Growth Facility. This unit is capable of a simple and rapid method for orienting crystals from a visual display of the spatial distribution of protons scattered from surface layers only a few tens or hundreds of atoms thick.

The unit is operational and a series of test samples are being investigated to determine the sample requirements for operation and the interpretation of the blocking patterns. Upon completion of the above tests, demonstrations of the use of the instrument for crystal orientation determinations and surface damage will be conducted. A technician is being trained to provide operational assistance for users of the instrument.

2. The facilities listed below, while not supported financially by the Materials Sciences Council, are available to participants in the MRL program who are in need of such services. Arrangements concerning their use are made directly between the individual desiring the service and the professor in charge of the facility.

Activation Analysis  N. T. Porile, Chemistry
Neutron Generator  N. T. Porile, Chemistry

The equipment listed below is, in general, associated with a particular staff member carrying out materials work at Purdue University. Although the equipment is not necessarily freely available and does not operate as a service, arrangements for use by specific researchers can be made (this is not a complete listing).
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Descriptions of Cluster Areas

1. **Production and Utilization of Phonons and Their Interactions with Matter and Radiation (Acousto-Optic, Acousto-Electric, and Ultrasonic Research)**

Research at Purdue in the above mentioned areas involves participants in the Electrical Engineering, Chemistry, and Physics areas and may be classified as follows:

a. Ultrasonic studies of solids. Properties studied include: elastic constants; electronic and lattice contributions to binding; electrical transitions; phonon-phonon, phonon-electron, and phonon imperfection interactions; piezoelectricity; charge transfer, and screening; and structural relaxation processes.
b. studies involving phonons generated by acousto-electric effect, hot charge carriers, and stimulated Brillouin scattering, including: optical modulation by intense phonon beams; microwave amplification by inverted phonon populations; phonon attenuation from light scattering; modulation of anomalous x-ray transmission by phonon beams; phonon dispersion.

c. acoustic surface waves studies including: propagation, steering, enhancement, nonlinear interactions.

d. applications of ultrasonics including: acousto-optic imaging, and flaw detection by application of random signal processing to ultrasonic pulses.

e. multiphonon relaxation of rare earth ions in crystals: implications for upconversion detection of 10 micron photons, and possibility of cooperative effects: supernonradiance.

2. Research for Elucidating Transport Phenomena in Well Characterized Oxides

There has been growing emphasis on gaining an understanding of the properties of metal oxides which are comparable to our understanding of the principles governing the behavior of "standard semiconductors" such as Ge or InSb. While a large number of models has been proposed to account for these observations, no completely satisfactory explanation of transport phenomena in oxides seems to be available. Currently, ten to twelve faculty members are engaged in full-time or part-time studies in this field, which encompasses both fundamental and applied research. Examples of nonroutine work include studies of band structures through ESCA and Auger spectroscopy, channeling phenomena, LEED studies of surface structures, tunneling through interfaces, use of Raman spectra as a means of studying lattice vibrations, photo-excitation effects, acousto-electrical and acousto-optical studies, and switching phenomena.
3. Frontier Research in Semiconductors and Semiconductor Devices

a. Frontier Research in Semiconductor and Metal Physics

The research in Solid State Physics at Purdue has exploited advances in technology, such as the development of the laser, superconducting magnets, Laser Raman Spectroscopy, extremely low temperature cryogenics, ENDOR, modern signal processing techniques, Mössbauer effect, and the use of infrared detectors. These studies have revealed new aspects of earlier problems, and uncovered new phenomena. There has also been a change in emphasis on the types and quality of the materials under investigation. For example, current research reflects the recent increased interest in semimetals, magnetic semiconductors, single crystal elemental semiconductors with closely specified impurity species and concentration, extremely pure metals, the intrinsic and extrinsic properties of alkali halides and silver halides, and in novel configurations such as semiconducting powders.

The diversity of current research interests in Solid State Physics both at Purdue and elsewhere suggests that increasing specialization characterizes the field. In such a situation, important progress continues to be made by internal development of new technology, or by adoption of current technology in examining the physical properties of new materials. Extension into extremes of such experimental parameters as temperature, pressure, magnetic field, and excitation, continue to be used as roads to new phenomena and important physics.

b. Semiconductor Devices

Because of the broad applicability of semiconductor effects to devices, the area of semiconductor devices is best classified as those materials studies which are motivated primarily by their applicability to a particular device, or class of devices.

Based on past experience the areas of interest will change quite rapidly as new understanding and effects are uncovered. At the present time, interfacial properties of semiconductors are under extensive study.
because of their importance in field effect transistors, charge coupled devices, and surface wave devices. Studies of the properties of amorphous semiconducting films which are necessary for the ultimate utilization of amorphous films as devices are also under study.

4. Modern Approaches to the Study of Interfaces and Interfacial Phenomena

The recent introduction at Purdue of several new and state-of-the-art experimental facilities which are primarily used in studying interfaces and interfacial phenomena has provided a new impetus to studies of surface phenomena. Two new items of equipment have been included as Central Facilities and are available for extensive use for materials science studies. These central facilities are the ESCA spectrometer under the direction of Professor J. W. Amy and the LEED-Auger equipment under Professor S. J. Hruska.

Research in this cluster area includes a wide spectrum of methods, including the above-mentioned equipment as well as ultrasonics, radio-tracer, sessile drop, electron microscopy, etc., which are available to characterize free surfaces and interfaces. Typical problems studied in this cluster area include catalysis, wetting and bonding, interface controlled mobility, solidification, nucleation, anomalous photovoltaic effects, electrical states at surfaces, and thin-film electrical devices.

5. Seed Cluster: Materials Sciences Research Relevant to Natural Resources

The needs for developing and improving processes for producing materials are becoming increasingly critical owing to depletion of high grade mineral resources, environmental pressures, conflicting and escalating energy demands, foreign competition, and other factors. In many cases, developments in this field are hampered by a lack of understanding of the behavior and properties of certain materials, either singly or in combinations. It is the intent of the Materials Sciences Council to seed research projects in this area provided that: (1) truly interdisciplinary
materials research of a high scientific quality is proposed; and (2) the utility of the expected results in materials processing or production is clearly demonstrated. Research has been initiated into certain aspects of recovery of high grade scarce metals using nonpolluting techniques, primarily by members of the Department of Geosciences.
CHANGES IN PERSONNEL

Changes among the roster of participants in the NSF-MRL Program were as follows:

Dr. N. S. Chung began employment with Professor R. L. Mieher of the Department of Physics in May, 1973 as a postdoctoral research associate. He received his Ph.D. degree from Purdue University.

Dr. D. A. Lilly, also of the Department of Physics, is working with Professor G. Ascarelli after receiving his Ph.D. in December, 1972 from Purdue University.

Dr. F. E. Richards began his postdoctoral appointment in October, 1972 working with Professor A. N. Gerritsen of the Department of Physics. He received his Ph.D. from the University of Chicago in 1972.

Dr. G. O. Deputy, previously engaged in research with Professor R. W. Vest of the School of Electrical Engineering, has received her Ph.D. and was appointed January 1, 1973 as Assistant Visiting Professor in the School of Materials Engineering.

Professor R. W. Vest was appointed Acting Head of the School of Materials Engineering on January 1, 1973, replacing Professor R. E. Grace who assumed full-time responsibilities as Head of the Division of Interdisciplinary Engineering Studies.

Professor E. P. J. Kartheuser of the University of Liège, Belgium, joined the Department of Physics on September 1, 1972 as a visiting professor. He is collaborating in research with Professor S. Rodriguez of the Department of Physics.

Dr. J. E. Robinson of the Argonne National Laboratory, was appointed visiting professor in the Department of Physics from May 7 to June 15, 1973. He worked in collaboration with Professor S. Rodriguez of the Department of Physics and presented a special series of lectures.
Professor A. W. Overhauser joined the Department of Physics as professor in August, 1973.

Dr. S. Bhagavantam of the Institute of Science, Bangalore, India, worked in collaboration as a visiting professor with Professor A. K. Ramdas of the Department of Physics from September 25 through October 13, 1972, presenting a series of lectures.

Dr. A. P. B. Sihha, Associate Director, National Chemical Laboratory, Poona, India, joined the Department of Chemistry on February 7, 1973 as a visiting professor and is collaborating in research with Professor J. M. Honig of the Department of Chemistry.

Professors on Sabbatical Leave:

Professor W. R. Robinson, Department of Chemistry, is on sabbatical leave from June 1, 1973 to December 31, 1973 with Professor C. T. Prewitt, Department of Earth and Space Sciences, State University of New York at Stony Brook, carrying out high temperature single crystal studies of metal oxide systems with interesting electrical properties.

Professor G. Ascarelli, Department of Physics, returned from sabbatical leave at the Laboratoire de Spectrométrie Physique, Faculté des Sciences, Grenoble-Gare, France.

Professor P. Fisher, Department of Physics, has returned from sabbatical leave from the Department of Physics of the University of Western Australia, Nedlands, Western Australia.

Professor J. K. Furdyna, Department of Physics, returned from sabbatical leave from the Polish Academy of Science of the Institute of Physics, Warsaw, Poland.

Professor F. J. Friedlaender, School of Electrical Engineering, returned from sabbatical at the Institut für Werkstoffe der Elektrotechnik of the Ruhr University, Bochum, West Germany.
Honors Received by Materials Scientists:

Professor N. T. Porile, Department of Chemistry, was awarded a John Simon Guggenheim memorial fellowship, September 1971 to August, 1972.

Professor R. J. Schwartz, School of Electrical Engineering, was awarded a NASA Certificate of Recognition.

Professor G. W. Neudeck, School of Electrical Engineering, received the D. D. Ewing award as outstanding teacher in Electrical Engineering; the A. A. Potter award for outstanding teaching in all Engineering Schools; and the Eta Kappa Nu outstanding Instruction Award in Electrical Engineering Honors.
ADMINISTRATION

The NSF-MRL Program was administered by a seven-member Materials Sciences Council. This Council is charged with the setting and implementation of policies and with the administration of facilities over which it has cognizance. All financial decisions are also made by the Council. Miss Cinda Edwards, Business Representative and Executive Officer to the Materials Sciences Council, is in charge of day-to-day operations.

Submitted by the Materials Sciences Council,

C. A. Angell
W. M. Becker
J. R. Cost
R. L. Gunshor
J. M. Honig, Chairman
R. J. Schwartz, Secretary
R. J. Sladek

Copies of this report may be obtained by writing to Professor J. M. Honig, Chairman, Materials Sciences Council, Physics Addition II, Room 285, Purdue University, West Lafayette, Indiana 47907.
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xxxı
Characterization of Amorphous Bi$_x$Ge$_{1-x}$ Thin Films (Anderson, Meininger, Neudeck, Liedl, and Hruska)

A series of Bi$_x$Ge$_{1-x}$ thin films have been formed by co-deposit vapor quenching onto liquid nitrogen cooled Corning 7059 substrates and then annealing in situ to 160°C. All films for which $x \leq 11$ atomic percent were x-ray amorphous.

Thermoelectric power measurements indicate n-type conductivity for all binary films and p-type conductivity for elemental germanium films. The electrical resistivity for all films closely follows a $\rho = \rho_0 \exp (T_0/T)^{1/4}$ dependence from room temperature to near liquid nitrogen. The resistivity appears to be independent of frequency from d.c. to 500 kHz.

Support: NSF-MRL
a provision for operation in the saturation or non-saturation-load mode. A set of high resolution photomasks was produced with the aid of computer assisted drafting. A fabrication process sequence was designed to realize the desired results and several samples were produced. These were then evaluated by examining the current-voltage, capacitance-voltage and drain-substrate p-n junction characteristics. The gate dielectric strength was also measured.

Support: School of Electrical Engineering, Purdue University

**Anomalous Photovoltaic Effect in Thin Films** (Anderson, Ma, Hruska)

Germanium thin films have been made at nitrogen pressures of approximately $10^{-7}$, $10^{-6}$ and $10^{-4}$ Torr and at oxygen pressures of approximately $10^{-6}$, $10^{-5}$ and $10^{-4}$ Torr. Angles of incidence of the Ge flux relative to the substrate plane were $15^\circ$, $23^\circ$, $30^\circ$, $45^\circ$, $60^\circ$ and $75^\circ$. Substrates are Corning 7059 held at $200^\circ$C during deposition.

Maximum photo-voltages are obtained for $10^{-4}$ Torr oxygen during deposition and $15^\circ$ angle of incidence of Ge flux. The magnitude and the sign of the photo-voltage both depend on the oxygen pressure during deposition and on the angle of incidence of the Ge flux. Varying amounts of nitrogen during deposition have negligible effect on the resulting photo voltage.

A gross structural model has been constructed to explain the observed phenomenon. This model is currently undergoing a critical examination.

Support: NSF-MRL
Publications:

Fundamentals of Vacuum Technology, a commercial, self-paced learning package employing a standard textbook, over 500 pages of supplemental notes and over 10 hours of video tape; designed and written by R. M. Anderson, copyright, Purdue University 1973.


Talks:


M.S.E.E. Thesis:

Computer Simulation of Glass Transition in Ionic Liquids (Cheeseman and Angell)

During the past year this investigation of the nature of the glassy state has been expanded to include computer simulation of the transition from fluid to configurationally arrested state by means of molecular dynamics calculations. In this endeavor we have collaborated with L. V. Woodcock of Cambridge University, England, who has developed a molecular dynamics computer program for the simulation of systems consisting wholly of ions. In this computation, interaction potentials are assigned to each type of ion pair in the system and, by a computation of the force acting on each particle at small successive instants of time, the complete time development of the system is calculated. By suitable choice of potentials, it has proved possible to calculate a radial distribution for the classical oxide glass, SiO$_2$, which is in excellent agreement with experiment. Furthermore, calculations of the diffusion coefficients for silicon and oxygen at temperatures beyond those accessible to direct experimentation, have been made. Similar data have been obtained for the glass-forming salt, zinc chloride, and for the silica analog, BeF$_2$. A report of these calculations to the recent Gordon Conference was very well received. It appears this approach to the study of liquid and glass state problems is full of promise, and will provide a powerful new tool to unravel the structural and dynamic problems presented by the glassy state.

Support: Purdue University
Study of the Glass Transition in GeO₂, Lithium Acetate and Sulfur Monochloride (Tucker and Angell)

The studies of the thermodynamics of the glass transition reported previously have been extended to include three interesting new cases, GeO₂, lithium acetate, and sulfur monochloride, S₂Cl₂. GeO₂ is interesting since it is closely analogous to the classical SiO₂ glass, the high glass transition temperature of which renders it inaccessible to precise experimentation. A thermal manifestation of the glass transition in GeO₂ had previously been considered unobservable, but, using the new high temperature differential scanning calorimeter provided as a central facility by the Purdue Materials Science Program, we have succeeded in determining directly the change of capacity for this interesting glass. The increase at the glass transition is quite the smallest yet found for any glassy material. Using existing heat of fusion data, it is found that some 70% of the entropy of fusion is retained in the glass. A striking contrast to this behavior is provided by the case of lithium acetate which exhibits a rather large change in heat capacity at the glass transition, and is found to have lost 90% of its entropy of fusion by the time the temperature has fallen to T_g. It appears that even in an infinitely slow experiment the glass transition for this substance would occur only 10 degrees lower in temperature than that observed experimentally. Sulfur monochloride was studied because it appears to be the simplest molecular liquid known to form a glassy phase. Its change in heat capacity at the glass transition like that of lithium acetate is quite large, but it appears to retain almost 50% of its entropy of fusion in the glass.

Support: NSF GP 30722

Thermodynamics of Disordering Transitions in Mixed Crystals (Ego1f and Angell)

In order to search for parallels in the behavior of disordering transitions (lambda-type) in crystals and disordering transitions (glass-type) in supercooling liquids, a study of the effect of changing composition in crystal systems in which one component exhibits a lambda-type transition
has been made. Three systems having sodium nitrate as one component in common have been studied. The most extensive measurements have been performed on the system NaNO\textsubscript{3} + AgNO\textsubscript{3}, in which solid solutions of AgNO\textsubscript{3} in NaNO\textsubscript{3} containing up to 60 mole % AgNO\textsubscript{3} are known to exist. The lambda transition which occurs in sodium nitrate at 549K is found in all the solid solutions, but the magnitude of the transition, and temperature of the heat capacity maximum, decreases systematically with increasing silver nitrate content. The entropy change associated with the transition is found to decrease linearly with mole % AgNO\textsubscript{3}, implying that each Ag\textsuperscript{+} ion added to the NaNO\textsubscript{3} lattice inhibits structural randomization of one nitrate anion. Similar studies have been performed in the system NaN\textsubscript{O} + KNO\textsubscript{3} and NaNO\textsubscript{3} + NaNO\textsubscript{2}. In the latter systems the effect of composition on the sodium nitrate transition is much more pronounced. In both cases the lambda form of the transition is destroyed, and excess heat capacity tends to develop at a much lower temperature. Measurements are to be extended to the study of kinetic behavior as a function of disorder.

Support: NSF GP 30722

Anomalous Heat Capacity of Supercooled Water and Solutions (Tucker and Angell)

Although water is not convincingly defined as a material, the nature of its properties as it is cooled below 0°C towards an eventual glassy state, is so unusual as to warrant reporting in this document. In order to check theories for water properties based on a random network model, methods of measuring the heat capacity in the temperature 0°C to -40°C have been developed. A technique in which water is inhibited from crystallization by dispersing it in emulsion form, has been utilized to determine the heat capacity to -40°C with an accuracy of ±5%. The heat capacity is found to commence an exponential increase at temperatures below -25°C, and by -39°C has increased to 80% above the normal value (1.0cal.gm\textsuperscript{-1}) The presence of a lambda-like transition at a temperature of approximately -45°C has been postulated to resolve an entropy paradox posed by this heat capacity behavior. It has been found that the heat capacity anomaly is
Compressibility of Supercooled Water (Speedy and Angell)

In view of the extraordinary heat capacity reported in the previous entry it has become desirable to determine the remaining unstudied thermodynamic intensive property of water in this region, the compressibility. This has been measured using a capillary technique in which the length of a column of water is studied as a function of pressure up to 100 bar (the bursting pressure of the glass pressure vessel). Compressibility data of 2% accuracy have been acquired in the temperature range +40°C to -26°C. These data also show an exponential rise in compressibility as temperature falls below 10°C, and data are fitted with a critical point type expression with a critical temperature of -45 ±3°C in agreement with the transition temperature postulated on the basis of the heat capacity study.

The homogeneous nucleation temperature of water emulsions has been studied as a function of pressure up to 2 kbar. It decreases rapidly with increasing pressure, reaching -80°C at 2 kbar.

Support: OWRR, NSF GP 30722
conductance and dielectric constant enter as parameters in the equations describing the dispersive characteristics of such two-phase systems, it was hoped that a proper analysis of the capacitance and conductance of carefully prepared emulsions as a function of frequency in the range 1 to $10^6$ Hz might permit the determination of these two interesting material constants down to temperatures as low as $-40^\circ C$. These efforts have met with only partial success. Very well defined dispersions in which the imaginary part of the dielectric constant shows almost the theoretical Debye form, have been obtained, with frequency maxima in the region anticipated from the known conductance of water at 0 and $25^\circ C$. However, the dispersion in these cases has proved too strong, leading to values of the dielectric constant for water (the dispersed phase) which are far too low. The origin of these difficulties has been associated with the formation of a capacitive layer of surfactant used in the emulsion preparation along the electrode walls, but it has not proved possible to properly compensate this effect. It seems at this point that the technique will prove ultimately unsatisfactory for the precise measurements of the quantities of interest and that other methods to determine the dielectric constant will need to be invented. This is important since it is very probable that water, at temperatures approaching $-40^\circ C$ will acquire an extremely large dielectric constant and appear to be passing into a ferroelectric transition with a transition temperature at $-45^\circ C$.

Support: NSF-MRL

**Protonically Conducting Glasses (Hodge and Angell)**

Apart from the interruptions incurred by the last mentioned new project, studies of protonic conductivity in glasses have proceeded systematically. Since the last report, extended studies of the effect of replacing protons with lithium ions have been conducted in the systems $H_2Zn_2Cl_7\cdot7H_2O + Li_2Zn_2Cl_7\cdotH_2O$. Very pronounced decreases in conductivity amounting to two to three orders of magnitude were found to follow the replacement of a part of the protons by lithium ions. This effect
would appear to confirm the protonic origin of the high conductivity of the pure acid glasses and suggest that the high conductivity of the acid glasses depends on achieving a suitable orientation of water molecules with respect to the anions of the glassformer in order to permit fast proton transfers. This arrangement is evidently interrupted by orientation of water molecules around lithium ions, leading to a very rapid decrease in conductivity associated with their addition. Conductivity studies of \( \text{H}_2\text{SO}_4-\text{H}_2\text{O} \) solutions have also been performed, and a correlation of the conductivity at \( T_g \) with the absolute value of \( T_g \) has found. As additional systems are studied a correlation between the magnitude of the conductance at \( T_g \) and \( T_g \) itself seems to be emerging as a general rule. This correlation suggests that if a strong acid with a glass temperature in the vicinity of room temperature could be produced, such a glass would have a conductivity of the order of 10\(^{-1}\) \(\Omega^{-1}\) \(\text{cm}^{-1}\). Such a substance would obviously have important materials applications in fuel cells and in electrolysis equipment as a solid electrolyte medium. It appears that such materials have already been invented since the sulfonic acid resins based on the fluorocarbon polymer skeleton which are utilized by G.E. for fuel cells, etc., has essentially the properties predicted by our extrapolation. It is expected that further study of the fundamental properties of proton conducting glasses in the absence of a polymer skeleton should help the understanding of the basic mechanism by which such high proton conducting materials operate.

Support: NSF-MRL

Proton Magnetic Resonance in Glass Forming Protonic Acids (Shuppert, Hodge and Angell)

A brief series of measurements in which the temperature-dependent line-broadening of the proton resonance in the glass-forming acid solutions which were the subject of the previous entry, has been carried out. The half-width of this resonance line in two systems, \( \text{H}_2\text{Zn}_2\text{Cl}_7.7\text{H}_2\text{O} \) and \( \text{Li}_2\text{Zn}_2\text{Cl}_7.7\text{H}_2\text{O} \) has been studied in order to determine whether the mobility of the protons in the first case can be characterized by pmr methods. Due to the rapid exchange between the "free" protons and the protons on the associated water
molecules, the differences in signal between the two solutions are not pronounced since the average is heavily weighted by the water molecules in each case. However, some distinction can be observed and, as expected, the line-broadening proceeds somewhat less rapidly in the protonic acid case. Unfortunately, a separate signal for the mobile protons has not been observed at the lowest temperatures, as originally had been hoped.

Support: NSF-MRL

Electrical Relaxation Studies in Viscous Ionic Liquids by Noise Techniques (Gammell and Angell)

As reported in the previous issue a program to study the absorption of electrical energy by determining the frequency dependence of the random voltage (Boltzmann noise) which they generate, has been underway in this laboratory. Most of the effort to this point has been expended on developing signal detection and data processing techniques by which the range of the method is extended using correlation of independent amplifiers to reduce the background noise and permit the sample noise to be studied over a wider resistance range. This is a complicated area in which progress tends to be slow. Dr. Gammell took leave from Purdue for three months to pursue the application of this technique to the study of relaxation in liquid crystals at the University of Southampton, with which the principle investigator collaborates under the auspices of the NATO joint research program. The amplifiers and the computer programs developed at Purdue for this project are currently remaining at Southampton in order that that project there can be brought to fruition following Dr. Gammell's return to Purdue. The study here is therefore suspended for the time being.

Support: NSF (GP 30722)

Publications:


Talks:


M. S. Theses:


Ph.D. Theses:

Optical Detection of Paramagnetic Resonance of the Self-Trapped Exciton in KBr (A. Wasiela*, G. Ascarelli and Y. Merle d'Aubigne*)

Paramagnetic resonance of the self-trapped exciton has been studied in KBr. The general features of the spectra confirm the validity of Kabler's model of a $V_K$ center having trapped an electron. The dependence of the optically detected E.P.R. signal on the direction of polarization of the light provides an important clue for the identification of the different E.P.R. lines.

Support: National Science Foundation GH33774

A Comparative Electron-Spin-Resonance Study of the Ground State and a Photoconverted Metastable State of the Mg$^+$ Donor in Silicon (Baxter and Ascarelli)

Magnesium diffused into silicon forms a deep-double-donor state. Depending on the compensation, the distinct valence states Mg$^0$, Mg$^+$, or Mg$^{++}$ are possible. EPR measurements have been performed at 55 GHz on the paramagnetic valence state Mg$^+$ at liquid-helium temperatures. In thermal equilibrium, with the sample in the dark, the EPR absorption of Mg$^+$ is consistent with the Mg$^+$ ion occupying the tetrahedral interstitial position, with $1s(A_1)$ as the electronic ground state. This confirms previous optical-absorption work. With near-infrared light incident on the sample ($1 < \lambda < 2\mu$), this paramagnetic center is converted to a metastable state (Mg$^+$)*, where the Mg$^+$ ion is displaced from $T_d$ to an interstitial position along the $\langle 111 \rangle$ axis of the Si unit cell. Although only a small g shift of Mg$^+$ results

* A. Wasiela and Y. Merle d'Aubigne are at the University of Grenoble.
from such a conversion, large changes are observed in both the contact interaction with the magnesium nucleus and the spin-lattice relaxation time. The optical conversion is total below $\sim 14^0K$, where the characteristic lifetime is of the order of minutes. In the dark, $(Mg^+)^*$ decays back to $(Mg^+:T_d)$ with second-order kinetics. This optical conversion can be explained either by an ionic-motion model or by an electron transfer process involving $Mg^{++}$ ions associated with a substitutional lattice defect.

Support: National Science Foundation GH33774

Piezo-Optic Study of the F Center in Alkali Halides Evidence for Structure in the F Band of KCl, KBr and NaCl (A. Perregaux and G. Ascarelli)

Using a piezo modulation technique, we have observed structure in the F band of KCl, KBr and NaCl; we call $F_I$ and $F_{III}$ the two bands responsible for this structure. It is noteworthy that the structure is observed only with light polarized perpendicular to the stress axis. We find an empirical relation defining the position of the K and L bands with respect to the F band. This relation applies to most alkali halides and corresponds to a model in which the states giving rise to the $F_I$, $F_{III}$, $K_1$, $K_2$, $L_1$, $L_2$, $L_3$ bands are states of a rigid rotator corresponding to odd quantum numbers. We suggest that such rotational states arise from a small $\Gamma_4^+$ distortion of the ions surrounding the F center vacancy. The magnitude of the ionic motion corresponding to odd lattice modes is limited to a nearly fixed value by a much larger distortion caused by the coupling of the $p$ like electronic states to $\Gamma_3^+$ and $\Gamma_5^+$ lattice distortions.

Support: National Science Foundation GH33774

The Influence of "Rotational" Lattice Deformation States on the Lifetime of the F Center (Ascarelli)

Recent Endor measurements of the relaxed excited state of the F center indicate that this state is $p$ like. Previous theories of the temp-
erature dependence of the radiative lifetime of the F center and of the Stark effect in emission were based on the assumption that the excited state is s-like with an admixture of the p-like states produced by the interaction with $\Gamma^{-}_4$ modes. The present model supposes a p-like excited state and a large lattice relaxation of $\Gamma^+_3$ symmetry. On account of the latter the ionic motion with $\Gamma^+_4$ symmetry takes place in a potential that resembles a square well and the spectrum of the $\Gamma^+_4$ modes is that of a rigid rotator. The excitation of the different rigid rotator modes gives rise to a temperature dependence of the radiative lifetime that is in excellent agreement with experiment.

The Stark effect can be explained as having both an electronic and an ionic component. The latter is very much enhanced by the local electric field produced by the change of the electronic charge distribution resulting from the applied field. The changes of lifetime produced by the applied field are primarily of ionic origin. They do not depend on the direction of polarization of the emitted light in agreement with the experimental result. The major difficulty of the model is that, contrary to the experimental result, it predicts no polarization of the emission. To explain the observed effect the selective population of some of the $|p_{1}\rangle$ states must be assumed during lattice relaxation.

Support: National Science Foundation GH33774

Far Infrared Resonance (Momin)

Mr. Momin built an HCN - H$_2$O laser capable of emitting about 20 mW at either 337 $\mu$m or 220 $\mu$m. The power is sufficiently stable so that the construction of a spectrometer appears promising.

Support: Material Research Laboratory
National Science Foundation GH33774
Publications:


Talks:


Operation of the Intermagnetics General Corporation (IGC) High Field Superconducting Magnet. (Ascarelli, Becker, and Lilly)

Recent tests of the magnet have been completed with the emphasis on improving heat exchange between the low temperature helium gas and the lead system. With leads disconnected, the boil-off rate is 0.5 liters/hr. With leads connected and zero field, the rate is \(-1.3\) liters/hr., and is approximately constant up to 11 tesla, increasing to \(-3.8\) liters/hr., at \(-14\) tesla. With the present system, the boil-off rates appear to be independent of details of the counterflow lead system.

Support: National Science Foundation GH 33774.

Transport Measurements Using the IGC Magnet (Lilly, Sohn, and Becker)

Magnetotransport measurements on pure Cd at 4.2°K and 1.4°K, and on high mobility p-type Ge at 77°K, have been carried out in fields up to \(-13\) tesla using the IGC magnet. The results on Cd show that the transverse magnetoresistance increases as \(H^n\) (\(n \approx 2\)) and that the Hall resistivity reverses sign below 4.2°K. This work is an extension of Ph.D. thesis results on intersheet scattering in Cd and Cd alloys. Magnetophonon oscillations have been reported in the literature for very pure p-Ge. Field modulation and phase sensitive detection techniques were employed in the present measurements. Although a sensitivity of 0.01% in the resistance was achieved, oscillations could not be seen in the best p-Ge locally available. This work is preliminary to an investigation of the stress dependence of the magnetophonon effect in p-type semiconducting crystals.

Support: National Science Foundation GH 33774.
Band Structure Changes in p-GaSb Under Uniaxial Compressive Stress
(Metzler and Becker)

The study and analysis of the galvanomagnetic properties of p-GaSb under uniaxial stress has been completed. Stresses up to $10^{10}$ dynes/cm$^2$ were employed in the investigation. The results at zero stress were analyzed in terms of conduction by two spherical parabolic bands. The stress results have been interpreted in terms of a model involving decoupling of the valence bands. Refinements of the model included the effects of stress-induced splitting of the impurity states and strain-dependent deformation of the energy surfaces. Although the models used could be made to fit both the low stress and high stress regions, a good fit could not be obtained over the entire range for a single set of parameters. Qualitative arguments indicated that the full theoretical form for the deformation of the energy surfaces, as given by Pikus and Bir, would lead to better agreement with the experimental results.

Support:  National Science Foundation
Materials Research Laboratory  GH33574

Hydrostatic Stress Effects in n-GaSb(Te) (Ru-Yi Sun and W. M. Becker)

In an extension of previous work, measurements of the transport properties of n-GaSb(Te) as a function of temperature have been carried out at high pressure. The results on a low concentration sample suggest that at low temperatures, for $P > P_s (< 8$ kilobar at $4.2^\circ$ K) the carriers in the $\Gamma$-minimum are all transferred directly into impurity levels associated with the L-minima, leading to impurity conduction. At high temperatures, for the same sample and $P(300^\circ$K) $> 10.7$ kilobar, electrons appear to be thermally excited from these states into the L-band. A donor ionization energy of $\epsilon_D = 13.8 \pm 0.2$ meV ascribed to impurity levels associated with
the L-band edge has been determined from the high temperature range of the resistivity curves. These results give the first measurement from temperature data of the activation energy of the Te level associated with the L-minima. Apparently anomalous increases with pressure in the resistivity, $\rho$, and in the activation energy for hop conduction, $\epsilon_3$, have been noted at low temperatures. These have been tentatively ascribed to compensation and to the presence of impurity states related to inequivalent bands. A complete survey of sample behaviors for Te-doped n-GaSb is in process.

**Support:** National Science Foundation
Materials Research Laboratory Program GH33574

**Publications:**


"Observation of Impurity Conduction Associated with the L-Minima in N-GaSb(Te)," Ru-Yi Sun and W. M. Becker, Solid State Communications (to be published).

**Talks:**


**Ph.D. Thesis:**

Brillouin Scattering Studies of Magnetoacoustoelectric Interactions  (Parker and Bray)

The work in this area was completed with the writing of the Ph.D. Thesis of T. Parker. A detailed study of the evolution of acoustoelectric domains in GaAs in the presence of transverse magnetic field, was carried out using the Brillouin scattering technique. In addition to observing the influence of magnetic field, significant improvements were achieved in instrumentation and technique, which provided major new insights into the linear and non-linear aspects of the growth of acoustic flux, and the evolution of the spectrum. The work covered three areas: (1) The effect of a transverse magnetic field ($\leq 25,000$ Gauss) on the acoustic flux growth in the weak acoustic flux regime; (2) A quantitative study of the mixing of acoustic waves, giving sum and difference frequency generation; (3) Effects of the magnetic field on the mixing of acoustic waves and on the flux-dependence of the acoustoelectric gain.

Support: National Science Foundation Grant No. GH 33344X and National Science Foundation - Materials Research Laboratory

Brillouin Scattering Studies of Phonon-Phonon Conversion in GaAs  (Wajda and Bray)

Objective: To study various phonon mode conversion processes by such means as: (a) reflection of phonons from crystal surfaces, (b) three-phonon interactions, (c) mode transformation through interaction with electromagnetic field. The purpose of such studies is: (1) to explore the conversion processes themselves. We are particularly interested in (c) where we wish to look for hitherto unobserved vertical transitions of phonons between the acoustic branches, involving microwave radiation
to provide the difference frequency; (2) to obtain high intensity acoustic flux in the various modes to better study the dispersion of different elasto-optic coefficients and other properties, such as ultrasonic attenuation.

**Experimental Procedure:** Very high intensity fast-TA flux propagating in the (110) direction is generated by means of acousto-electric amplification. Brillouin scattering allows us to see this mode, as well as LA and slow-TA modes. The different modes can be readily distinguished by their polarization conditions and different velocities. Relative intensities of the different modes can be measured.

**Progress and Present Status:** (1) Conversion of fast-TA phonons into LA and slow-TA modes by reflection of the acoustoelectrically-amplified domain from the anode end of the sample was observed. Such a way of generating slow-TA phonons was never reported before for GaAs.

The reflected acoustic flux was found to be produced in a large angular cone as opposed to the narrow cone of the incident flux. This fact allowed us to explain observations of apparent violation of light scattering polarization conditions by low frequency slow-TA phonons as due to strong contribution from off-axis flux.

This phonon conversion technique is being used now to measure ultrasonic attenuation of slow-TA and LA phonons. Attenuation data for slow-TA phonons in the frequency range of 0.3 to 3 GHz does not exist in the literature. The preliminary results show \( f^{1.5} \) dependence of attenuation on frequency.

(2) The calculation of dependence of the different phonon modes on elastooptic coefficients \( p_{11}, p_{12}, \) and \( p_{44} \) was done for various propagation directions. This combined with the experimental realization of phonon conversion permitting the production of slow-TA and LA phonons from strong fast-TA flux opens the way to separation of \( p_{11}, p_{12} \) and \( p_{44} \) and determination of their spectral dispersion.

(3) Group-theoretical calculations show that fast-TA phonons are allowed to decay into slow-TA and LA modes through interaction with microwaves. Mechanisms involved in such transitions were also studied. Experiments to search for these transitions are under way.
Acoustoelectrically-controlled Stimulated Brillouin Scattering (Mishra, Miller and Bray)

Objective: To use the acoustoelectric interaction to control acoustic phonon population and lifetime, and thereby control the threshold and required interaction length for achievement of stimulated Brillouin scattering (SBS). Achievement of such control would (1) permit study of SBS at lower power levels, without interference from other non-linear phenomena, and (2) provide new intense sources of, narrow, high frequency phonon beams.

Approach: The initial approach is to look for SBS in the back-scattering configuration, using acoustoelectric domains to provide an initial, strong back-scattered beam, and acoustoelectric amplification to enhance the phonon lifetime.

Progress and Problems: The major problem is to achieve simultaneously, strong acoustoelectric gain and strong Brillouin scattering cross section. Unfortunately, for the heavily-favored acoustoelectric amplification of fast TA (110) phonons, the backscattering cross section is zero. We therefore have to search for other compromise phonon modes that can satisfy the two criteria. Weaker amplification is possible for LA (111) modes and quasi-fast TA modes with momentum vectors 30° away from (001) toward (110) direction. Attempts to amplify these modes have thus far failed, because of competition from off-axis fast TA (110) phonons. Several procedures have been tested and new ones are being developed to shift the balance in favor of the desired modes, including 1) the use of transverse magnetic field, 2) control of sample cross section dimensions to discourage off-axis flux, and 3) resonant voltage pulsing techniques, whereby the amplifying voltage frequency is tuned to the transit time of the desired phonons over several round trip passages over the sample length.

Support: National Science Foundation - Materials Research Laboratory and National Science Foundation No. GH 33344X
Modulation of Raman Scattering (Abramsohn and Bray)

Objective: The major objective of this study is to obtain controlled modulation of the first and second order phonon Raman spectrum in piezoelectric semiconductors.

Methods of Attack: (1) Changing the optical phonon population by hot carrier generation directly affects one- and two-phonon Raman scattering. This has previously been accomplished by optical excitation of the carriers. We plan to test the efficiency of modulating the optical phonon population with hot carriers produced by high electric fields. (2) Modulating the acoustic phonon population by acoustoelectric amplification is known. Now we plan to determine the effect on the Raman two-phonon (optical and acoustic phonon) scattering, of modulation of the acoustical phonon population. (3) We shall also look for the effect on the first order Raman scattering cross section of the high fields and strains which occur in the acoustoelectric domains.

Purpose: (1) Modulation techniques and enhanced phonon populations should provide greatly improved sensitivity for Raman scattering studies, and enhance the detection of the weak Raman-shifted frequencies in the presence of the intense laser excitation frequency. (2) The use of Raman scattering data to study which optical phonons relax hot carrier energy may supply important physical information on the relative coupling strengths of the carriers to the longitudinal and/or transverse optical phonons. (3) The effect of the acoustoelectric domain on the Raman spectra of piezoelectric crystals should provide new insight into local fields and strains within the domain. The observance of modulated two-phonon Raman scattering could also provide insight into the phonon-phonon interactions in these crystals.

Progress: The program is in the planning stage, and the equipment for the experiments is being assembled. A double monochromator (Spex 1402) has been obtained and set up. Techniques for generating hot carriers and acoustoelectric domains are available.

Support: National Science Foundation Grant No. 33344X
Publications:


Sum and Difference Frequency Generation in Acoustoelectric Domains in GaAs, T. E. Parker and Ralph Bray, Physics Letters, to be published.

 Talks:


Ph.D. Theses:

Bleustein-Gulyaev Waves with Electronically Variable Phase Velocity
(Ho and Chen)

Objective: To vary the phase velocity of Bleustein-Gulyaev waves by interacting the waves with drifting charge carriers in an adjacent semiconductor layer.

Approach: The change in phase velocity of Bleustein-Gulyaev waves resulting from its interaction with drifting charge carriers is measured experimentally and compared with theoretical calculation.

Progress: A technique capable of producing large variation in phase velocity is studied. The scheme is to interact Bleustein-Gulyaev waves with the drifting charge carriers of a thin semiconductor layer. By matching the impedance at the interface of the semiconductor and the piezoelectric substrate, an exact dispersion relation is obtained. Our calculation shows that large and continuous variation in phase velocity can be achieved electronically if the adjacent semiconductor layer is thin and a proper piezoelectric substrate is used.

Experimental devices are fabricated using PZT-4 ceramics and commercially available Si-on-Sapphire wafers. The Si layers are about 1µ thick with resistivity in the range of 10~200 ohm-cm. A liquid layer is sandwiched between Si wafer and PZT to increase the coupling. The experimental data is in agreement with the theoretical calculation.

Support: NSF-MRL, David Ross Grant, Purdue Research Foundation

Acoustic Surface Waves Circulating Around the Periphery of a Piezoelectric Cylinder (Chen)

Objective: To study the modes and propagation characteristics of acoustic surface waves circulating around the periphery of a piezoelectric cylinder.
Approach: An exact dispersion relation is derived. Asymptotic solutions and numerical solutions are obtained.

Progress: The characteristics of electroacoustic surface waves supported by a curved piezoelectric-vacuum boundary are studied. A coaxial structure with a piezoelectric insulator as the inner cylinder and an electric conductor as the outer cylinder is considered. A dispersion relation for electroacoustic surface waves circulating around the periphery of the piezoelectric cylinder is obtained. Asymptotic solutions are compared with numerical solutions. Profiles for the mechanical displacement and electric potential for various modes are obtained. Possible application as delay lines with long-time delay is also studied.

Support: NSF-MRL, David Ross Grant, Purdue Reserch Foundation

Publications:

Talks:
X-Ray Determination of Valence Electron Charge Density in III-V Crystals: Indium Antimonide. (Bilderback, Colella)

For the Zn-Se structure $A_{III} B_V$, the f.c.c. reflections of the form $h+k+l=4n+2$ ($n = 0, 1, 2,...$) involve the difference between the $A_{III}$ and $B_V$ scattering form factors. Since the core charge densities are very similar for $A_{III}$ and $B_V$, a large fraction of the measured intensities is contributed by valence electrons. The core contribution can be accurately evaluated using Hartree-Fock (free-atom) wave functions. Therefore any departure from spherical symmetry of the valence electrons is expected to produce appreciable effects on the measured intensities. Eight quasi-forbidden reflections have been measured on In-Sb single crystals using Cu-Kα radiation, in the region $0 < \sin \theta/\lambda < 0.51$. Particular attention was paid in order to avoid multiple diffraction effects. A few "normal" reflections ($h+k+l = 4n$ or $2n+1$) were also measured and their intensities were in very good agreement with dynamical theory. The quasi-forbidden reflections on the contrary were 20-45% more intense than the free atom values. Furthermore, the (222) and ($\bar{2}\bar{2}\bar{2}$) differed by 26% whereas they should be equal for the Zn-Se structure. The (222) intensity can be different from ($\bar{2}\bar{2}\bar{2}$) if an interstitial charge is placed between neighboring atoms. However this asymmetry was not observed for (622) and ($\bar{6}\bar{2}\bar{2}$). The high values observed for the (200) and (600) can be interpreted as due to: i) an ionic charge transfer from In to Sb, ii) an interstitial charge placed off center along the bond. A least square refinement based on a gaussian distribution for the valence charge density provides a description in qualitative agreement with a theoretical contour map obtained by pseudopotential calculations. However, the structure factors resulting from these calculations are still much greater than the experimental values.

Work is in progress along two lines: i) repeat these measurements at different temperatures < 298°C, and ii) interpret our results in terms of a model in which any departure from spherical symmetry of the valence electrons...
Multiple Diffraction of X-Rays and the Phase Problem (Colella)

The general theory of n-beam x-ray diffraction (n > 2) has been developed in the framework of classical dynamical theory and applied to the Bragg case. It is shown that the crystal wave-vectors are the eigenvalues of a $4n \times 4n$ dispersion matrix. The boundary conditions are applied to a parallel sided crystal slab and show that for an infinite thickness only $2n$ wave fields survive. The Umweganregung plot of Ge (222) with Cu-Kα radiation has been considered in detail. The integrated intensity of an Umweganregung peak is defined here as a double integral with respect to $\Theta$ (angle of incidence) and $\phi$ (azimuthal angle). The (222-113) and (222-113) absolute integrated intensities were measured on a dislocation-free Ge crystal. Excellent agreement is obtained between experimental and calculated values. The ratio between the two integrated intensities (of the order of 7) did not change appreciably for a Ge mosaic crystal, although both reflections exhibited considerable increases with respect to the perfect crystal values. Since the two Umweganregung peaks considered in this experiment involve crystallographically equivalent reflections with different phases, it is suggested that the present technique can in principle be used for phase determination in crystal structure analysis.

$^1$)Intensity vs. $\phi$ plot, where $\phi$ is the rotation angle around the diffraction vector, and the angle of incidence $\Theta$ is constant, for the (222) reflection (Bragg case).

Support: National Science Foundation - Materials Research Laboratory
GH 33574

is represented by means of third and sixth order Kubic Harmonics.


$^2$)Private Communication.

Support: National Science Foundation-Materials Research Laboratory
GH 33574; National Science Foundation GH 39200
X-Ray Diffraction Studies of Acoustoelectric Phonons  
(LeRoux, Colella)

An x-ray spectrometer of special construction has been designed and built for measuring the anomalous transmission of x-rays in a crystal immersed in liquid nitrogen, located between the poles of a magnet. The unit has been tested satisfactorily. Acousto-electric phonons are produced in a n-type indium antimonide crystal, in which anomalous transmission of x-rays has been observed. Preliminary results, in absence of phonons, indicate a fairly good agreement between experimental data and predictions based on dynamical theory of x-rays. When acousto-electric phonons are produced the diffraction peaks are appreciably reduced (by a factor of 2) and broadened. These results indicate that the effects of phonon-photon interaction in our experiment are very well measurable.

Work is in progress in order to improve the experimental conditions and provide an interpretation of these results.

Support: National Science Foundation - Materials Research Laboratory GH 33574

Publications:


"Multiple Diffraction of X-Rays and the Phase Problem", by R. Colella (in preparation).

Talks:

Interstitial Solute Interactions and Diffusivity in Metals (Tewari and Cost)

A predicted relaxation of interstitial solute atoms following application of hydrostatic stress has been measured for the first time during the past year. The demonstration and measurement of this hydrostatic relaxation provides a new method for studying the behavior of interstitial solutes in solids. This method will compliment the more conventional (Snoek) relaxation studies by providing information concerning the reactions (as opposed to the rearrangements) of interstitial atoms.

In this study, isothermal measurements at 81.6°C of an anelastic relaxation induced by hydrostatic stresses in the range from ambient to 80,000 psi (5.52 Kbar) have been made for a Nb-2.3 at% O alloy. Analysis of the relaxation is made by both considering the relaxation spectrum to be composed of three discrete relaxation times and to be a lognormal distribution about some mean relaxation time. The relaxation which occurs during pressurization is considered to be due to the reaction of single interstitial oxygen atoms to form oxygen doublets (or higher order multiplets). The reverse reaction is considered to occur during pressure release. The relaxation strength and rate are found to be in good agreement with rough predictions based upon the above model for the reaction. The pressure dependence of the relaxation rate gives an apparent activation volume of 4 cm³/mole.

Support: NSF/MRL, GH 33574
Behavior of Inert Gases in Metals (Johnson and Cost)

The general goal of this project has been to apply new techniques to the study of inert gas-metal systems, with emphasis upon helium. Two specific problems which have received emphasis are that of the determination of the site occupancy (interstitial or substitutional) of helium atoms in the metal lattice and the investigation of the kinetics of bubble coalescence. Both of these problems are important in the design of nuclear power systems where nucleation and subsequent coalescence of inert gas bubbles can limit the efficiency of fuel burn-up.

Studies of the first problem, that of site occupancy, have been on the Al-He, Nb-He, and Cu-He systems. Results indicate that in the first two of these systems helium has substitutional occupancy, while in copper there is interstitial occupancy.

The investigation of the bubble coalescence problem has made use of comparisons between computer simulated coalescence and the actual coalescence as observed by electron microscopy. We find that bubble coalescence occurs at much slower rates than predicted. From this it is concluded that bubble mobility is not simply determined, as was previously believed, by the surface diffusion of metal atoms at the bubble interface. Some other mechanism, possible the nucleation of facets on the surface of bubbles, appears to be rate-limiting. Computer simulation studies of the facet-nucleation model are in reasonable agreement with experimental results, but a definitive test of this model has not yet been made.

Support: AEC, AT (11-1) 1799
Interfacial Properties of a Graphite Fiber-Magnesium Composite (Zimmer and Cost)

The initial objective of this research is to prepare and then determine the mechanical and interfacial properties of a graphite-magnesium fiber composite. A final objective is to optimize the mechanical characteristics of the graphite-magnesium interface by the study of controlled additions of solutes which promote wetting and interface adhesion.

The design of this composite requires that solutes which are carbide formers be added to magnesium to produce bonding with the graphite fibers. Investigations of various amounts of zirconium solute indicate that wetting and bonding take place and that this composite can be fabricated. Several samples have been prepared and preliminary mechanical tests have been made. A problem exists because wetting does not always occur completely throughout the samples and some porosity is also present. Present studies are being directed toward solving this problem.

Support: NSF/MRL GH 33574

Publications:


Talks:


Spectroscopic Studies of Electrolytic Solutions and the Low Temperature Glasses Formed From Them (Edgell, Barbetta, Pang, Rapp, Lee, and Kuriakose)

Efforts have been devoted to the development of a basic quantum theory of non-aqueous electrolytic solutions and the low temperature glasses formed from them. Studies continue on the structure at ion sites. These have included continued development of experimental and interpretative methods which bring the art to the point where it can detect and characterize ion sites present at 1% of the total population. Work continued on the detection and characterization of (structure at) ion sites for alkali metal and $\text{Tl}^+$ salts of $\text{Co(CO)}_4^-$ and $\text{NO}_3^-$ in a variety of non-aqueous solvents. The direct relation of these sites to chemistry in solution was demonstrated by identifying the ion sites where the reaction

$$3\text{TICo(CO)}_4 + 3\text{PPh}_3 \rightarrow \text{TI(CO(CO)}_3\text{PPh}_3)_3 + 2\text{Tl} + 3\text{CO}$$

takes and those where it can not take place. Studies of this type were carried out at a variety of lower temperatures (to 80°K) as well as at room temperature. The details of the frequency distribution of the intensity associated with vibration localized in the $\text{Co(CO)}_4^-$ ion were investigated for ion sites of simple solution structure and their interpretation in terms of linear response theory is in progress. The
measurements, which characterize the Co(CO)₄⁻ ion-solvent interaction in these systems, show major (quantum) differences in their dynamic behavior from that which seems to be characteristic of pure liquids, e.g. liquid CH₄. Progress was made in understanding the local, ion-translation modes in solution. Total forces acting on the ion were obtained from measurements and improvements made in the model for this motion. Efforts were made in improving the experimental measurements. Results were interpreted in terms of linear response theory. On the instrumentation side, the laboratory computer arrived and work was devoted to its assimilation. The interface to the Houston plotter was designed and built. The software required for its operation was written and this phase of our work has been transferred from the University Computer Center to the laboratory. The interface to the Raman spectrometer was designed and built. The first stage software for the operation of this instrument, including the basic drivers, has been written.

Support: NSF - GP 27928
       NSF/NSF
       PRF/XR

Excitons and Metal-Metal Bonding (Edgell, Lurix, Curry)

Librational spectra of "larger" molecules (e.g. Fe(CO)₅) do not follow theory based on the point-group symmetry of the molecule. Previous work on this project lead to the development of group theoretical methods for treating these molecules. Work aimed at the application and development of this theory was devoted to the study of the infrared and Raman spectra of liquid acetone and the infrared spectrum of tetramethylcyclo-
butane, 1,3-dione. Methods developed for the detection of ion sites in solution (see above) were applied. Small deviations from a simple form of the effective potential energy were found in each case and the results are being interpreted in terms of the local-mode theory for the vibration of larger molecules. In the course of this work, "third generation" software program was developed for the resolution of a complex spectroscopic band into its components. This program is written for the laboratory computer and is interactive between the operator and the computer. Effort was also spent on the interpretation of the infrared and Raman spectra of Fe(CO)$_5$ in the pure liquid and in concentrated solutions in terms of the kind of molecule sites (species) present in the condensed phase using the methods developed for the ion site studies (see above).

Support: NSF-MRL

Publications:


Talks:


"Relaxation Studies of Alkali Ion Motion in Ionic Solutions". W. F. Edgell, Fourier Transform Users Group Meeting, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 6, 1973 (invited).

"Structure in Electrolytic Solutions". W. F. Edgell, Coblentz Society Symposium on Application of Infrared and Raman Spectroscopy to Structural Problems in Chemistry (1/2 day; 3 speakers), Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 8, 1973 (invited).

Ph.D. Thesis:

"Electrolytic Solution Characteristics by Molecular Spectroscopy".

Far Infrared Recombination Emission in Semiconductors  (Fan and Thomas)

Studies of far infrared radiation, wavelength longer than 100 microns, emitted by germanium and GaAs semiconductors have been completed. The emission accompanies the impact ionization of a shallows impurity in the material. Germanium with Sb, As, or P impurity and epitaxial GaAs with an unidentified donor impurity have been investigated. Emission spectra measured with a Michelson interferometer show sharp peaks and a broad band. The sharp peak are produced by electron transitions between impurity states which have been identified in each case. The broad band is produced by transitions of conduction electrons to the impurity states. Information on the electron occupation of impurity states and energy distribution of conduction electrons has been obtained for conditions under impact ionization.

Support: ARO-D DA-ARO-D-31-124-72-G156

Optical Studies of Magnetic Semiconductors  (Fan and Chou)

The near ultraviolet absorption edge was found to exhibit a red shift in MnO and a blue shift in α-MnS and CoO₃ at the magnetic transition temperature. The three crystals are all cubic in structure and undergo an antiferromagnetic transition at the Neel temperature. A theoretical interpretation of the observed effect has been worked out which satisfactorily accounts for the experimental observation. Lattice distortion associated with the transition and electron-magnetic ion exchange interaction are both taken into consideration. The absorption edge is considered to be associated with electron excitations from the magnetic ions to the conduction band. For MnO and CoO, it is essential to consider the excited conduction electron to be localized around the magnetic ion.
Multiphoton Effects in Semiconductors (Fan and Lee)

Two-photon absorption has been measured using Nd-glass laser at light intensities up to $22 \text{ MW/cm}^2$. ZnTe was measured at temperatures 100-375°K. GaAs and InP were measured at 298°K and 15°K. Theoretical calculations have been made taking into account the valence band degeneracy, a second conduction band and, most importantly, the exciton effect. Transitions between states of various exciton series were considered. The calculated and experimental results for ZnTe are in good agreement in magnitude and in temperature dependence. For GaAs and InP, the agreement in magnitude is within a factor of 5, and the agreement between the calculated absorption ratio at the two temperatures and the experimental ratio is satisfactory.

Publications:
"Optical and Magnetooptical Absorption in Pure HgTe", A. S. Saleh and H. Y. Fan, phys. stat. sol. (b) 53, 163 (1972).

Talks:

Ph.D. Theses:

A piezospectroscopic study of the excitation lines from the \( \Gamma_8 \) ground state to the first two \( \Gamma_8 \) excited states of the \( p_{3/2} \) series of boron, aluminum, and indium (lines 1 and 2) and to the first \( \Gamma_6 \) excited state of boron (2p' line) has been made for compressive force \( \vec{F} \) along \( \langle 111 \rangle \), \( \langle 100 \rangle \), and \( \langle 110 \rangle \). The shear deformation potential constants of the excited states and the ground state of \( \Gamma_8 \) symmetry have been determined from these measurements. The results for boron acceptors, taken together with the theoretical calculations of Bir, Butikov, and Pikus, yield the shear deformation potential constants of the valence band of silicon \( \text{viz.} \) \( b = (-1.92 \pm 0.05) \text{ eV} \) and \( d = (-4.84 \pm 0.10) \text{ eV} \). Level crossing effects have been observed associated with the \( \Gamma_5 + \Gamma_6 \) sublevels of the excited states of lines 1 and 2 for \( \vec{F} \parallel \langle 111 \rangle \); nonlinear dependence on stress and stress dependent intensity changes have been observed for the stress induced components which have these \( \Gamma_5 + \Gamma_6 \) final states.

Support: National Science Foundation (CH 32001), National Science Foundation - Materials Research Laboratory (CH 33574), and Purdue Research Foundation

Excitation Spectrum of Bismuth in Silicon (N. R. Butler, P. Fisher, and A. K. Ramdas)

The excitation spectrum of bismuth donors in silicon has been studied under higher resolution than previously. All lines, except the 2s, reported before, have been observed together with five new excitations.
identified as the $4s$, $4f_0$, $4f_\perp$, $5f_0$, and $6p_\perp$ by comparison with calculated values. The energies of these lines are 68.09, 68.02, 69.07, 69.31, and 69.88 meV, respectively. The $4s$ and $4f_0$ excitations have not been observed for other donors. There is little indication of the $2s$ line presumably due to the low concentration of bismuth ($\sim 2 \times 10^{15}$ cm$^{-3}$) in the sample used. The $3d_0$ line is unusually broad as is the $2p_0$ excitation. The shape of the latter has been studied as a function of uniaxial stress. This has the effect of producing stress-induced $2p_0$ components which can be moved in and out of resonance with an optical phonon. Comparisons are being made between computer fits to the data and the theoretical line shapes of Rodriguez and Schultz; such fits will yield coupling parameters for the resonance interaction. As expected, it is found that as the $2p_0$ components go out of resonance they become comparable in sharpness to the other excitation lines. This is in contrast to the behavior of the $2p_\perp(-)$ component which, when caused to coincide with the optical phonon, fails to broaden; this is being studied further.

Support: National Science Foundation - Materials Research Laboratory (GH 33574) and National Science Foundation (GH 32001)

Solid State Spectroscopy in the Far Infrared (Chandrasekhar, Fisher, Momin, and Ramdas)

The Fourier transform spectrometer has been modified by moving the fixed mirror to double the total scan of the movable mirror; thus doubling the resolution. The performance has been tested on using the pure rotational water vapor spectrum. A program has been initiated to study the following: low frequency vibrations in $\alpha$-quartz, localized modes of oxygen impurities in silicon and germanium, and excitation spectra of donors and acceptors in semiconductors.

Support: National Science Foundation GH 32001; National Science Foundation - Materials Research Laboratory GH 33574 and Purdue Research Foundation.
Publications:


See also Ramdas and Rodriguez; Fisher and Rodriguez; and Rodriguez.

Talks:


See also Ramdas and Rodriguez; Fisher and Rodriguez; and Rodriguez.

Ph.D. Theses:

Energy States of Group III Impurities in Germanium (Soepangkat, Fisher, and Rodriguez)

A study has been made of the transverse Zeeman effect (Voigt configuration) of the excitation spectra of boron and thallium impurities in germanium, with the magnetic field, $\mathbf{B}$, along \langle100\rangle, \langle111\rangle or \langle110\rangle and using linearly polarized radiation. The results have been compared with the calculations of Lin-Chung and Wallis and the theory of Bhattacharjee and Rodriguez. The $g$-factors given by the former authors have permitted one case out of thirty-two possibilities to be selected for $\mathbf{B} \parallel \langle100\rangle$. Consequently, the $g$-factors of several of the states of both impurities have been found. The values obtained for the principal $g$-factors, $g_1$, $g_{3/2}$, of the ground states are $-1.53 \pm 0.09$ and $0.03 \pm 0.04$, respectively, for boron, and $-1.4 \pm 0.7$ and $0.23 \pm 0.04$, respectively, for thallium. The values of $g_D^{1/2}$ and $g_D^{3/2}$, for example, the $g$-factors of the excited state of the D line are $-6.14 \pm 0.13$ and $0.07 \pm 0.03$, and $-5.7 \pm 0.2$ and $0.06 \pm 0.23$, for boron and thallium, respectively. The difference in value between $g_3^{1/2}$ of boron and thallium is taken to be due to the difference in ground state wave functions of these two impurities, i.e., a manifestation of the chemical shift. The excited states have essentially the same $g$-factors as is to be expected for effective-mass-like levels. The quadratic factors have not been determined separately for each state. The relative intensities of the D components for $\mathbf{B} \parallel \langle100\rangle$ are in good agreement with theory. From the results obtained for $\mathbf{B} \parallel \langle100\rangle$, it is possible to predict the linear splittings and relative intensities of the Zeeman components for $\mathbf{B} \parallel \langle111\rangle$ and $\mathbf{B} \parallel \langle110\rangle$. Good agreement is found with the experimental results for the D components under the latter orientation; the agreement is not as good for $\mathbf{B} \parallel \langle111\rangle$. Some success is obtained in the interpretation of the C line for all three orientations if this is taken to be due
mainly to an excitation to the $\Gamma_7$ state of the $\Gamma_7 + \Gamma_8$ combination predicted by the effective-mass theory. The behavior of the G line has not been well understood.

Support: National Science Foundation GH - 32001; National Science Foundation GH - 33774; National Science Foundation - Materials Research Laboratory Program 33574.

Energy States of Singly Ionized Zinc in Germanium (Barra, Fisher, and Rodriguez)

This work represents the experimental part of a piezospectroscopic study of the symmetries and deformation-potential constants of the energy states of singly ionized zinc in germanium. From the behavior of the excitation spectrum of this impurity under uniaxial compressions along the $\langle 111 \rangle$ and $\langle 100 \rangle$ directions, symmetry assignments have been made for the ground state and the excited states of the C and D lines, and it is found that $d' = -2.18 \pm 0.06$ eV, $d'_D = 0.15 \pm 0.03$ eV, $b' = -0.65 \pm 0.03$ eV, and $b''_D = 0.61 \pm 0.02$ eV, where these are deformation-potential constants for the ground state of the impurity and for the excited state of the D line. These conclusions were reached by making a detailed comparison of the experimental results with the theory and were corroborated by similar measurements with compression along a $\langle 110 \rangle$ axis.

Support: National Science Foundation GH - 32001; National Science Foundation GH - 33774; National Science Foundation - Materials Research Laboratory Program 33574.

Publications:


See also Fisher, Ramdas and Rodriguez.

Talks:

"Piezospectroscopy of Singly Ionized Zinc in Germanium", P. Fisher, colloquium given at the Department of Physics, University of Western Australia, April 12, 1973.


"Spectroscopic Studies of Impurities in Germanium", P. Fisher, colloquia given at the Department of Physics, Wollongong University College, August 30 and September 4, 1973.

See also Fisher, Ramdas and Rodriguez.
Ph.D. Theses:


"A Spectroscopic Study of the Symmetries and Deformation-Potential Constants of Singly-Ionized Zinc in Germanium", F. Barra (deceased), to be awarded posthumously.
Consequences of Non-Zero Displacements of the Promoting Modes in Radiationless Relaxation (Fong and Wassam)

Recently, Nitzan and Jortner (NJ) treated the problem of radiationless relaxation from a single vibronic level in large molecules in the Born-Oppenheimer (BO) adiabatic approximation. The kinetic energy operator was employed as the perturbation coupling Hamiltonian. The assumption of zero-displacement parameters for the promoting modes was made. This assumption appears to be based on (a) the observation that for the benzene molecule in the low-pressure gas phase, only the totally symmetrical C-C skeletal and C-H stretching modes exhibit significant shifts of their equilibrium displacement in the $S_1 \rightarrow T_1$ transition and (b) the supposition that benzene in the gas phase retains its $D_{6h}$ symmetry in the excited triplet state. The last point is still questionable since it is well established that the lowest excited states of benzene in the crystalline state are in fact non-hexagonal and nonplanar. Nuclear configurational changes in excited
electronic states abound in the literature, and in general the NJ assumption of zero displacements for the promoting modes appears to be unjustified.

**Support:** ARPA Grant No. DAHC15-70-G-8

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**Cooperative Radiationless Relaxation** (Miller and Fong)

The theory of cooperative nonradiative multiphonon relaxation by a multi-atom system is developed in the framework of the adiabatic approximation in analogy with the Dicke theory of superradiance. As a concrete example, the nonradiative decay of impurity centers doped in a crystal lattice is considered. The assumptions underlying the theoretical development and the possibility of the experimental realization of this effect are discussed.

**Support:** ARPA Grant No. DAHC15-70-G-8

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**Energy Transfer Upconversion in LaF$_3$:Pr$^{3+}$** (Zalucha, Wright, and Fong)

Studies of infrared quantum counter upconversion in LaF$_3$:Pr$^{3+}$ and LaCl$_3$:Pr$^{3+}$ have led to the discovery of a process in which a red excitation photon results in the emission of a blue photon. When the $^1D_2$ level of Pr$^{3+}$ is excited by a cw rhodamine 6-G dye laser, blue fluorescence from the $^3P_0$ level is observed. From the flux dependence and lifetime of the induced fluorescence, we conclude that the observed phenomenon arises from
excitation annihilation involving pairs of ions in the $^3H_6$ and the $^1D_2$ states.

**Support:** ARPA Grant No.: DAHC15-70-G-8

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**Optical Study of Ion-Defect Clustering in CaF$_2$:Er$^{3+}$ (Fong, Fenn, and Wright)**

The effect of ion-defect clustering in CaF$_2$:Er$^{3+}$ has been investigated by means of fluorescence spectroscopy and lifetime measurements. The fluorescence spectra of CaF$_2$:Er$^{3+}$ exhibit a sensitive dependence on the dopant concentration and on the temperature history of the crystal. At low concentrations ($< 0.01$ mole%), only fluorescence lines arising from single Er$^{3+}$-F$^-$ interstitial pairs are observed. As the concentration increases, a large number of new lines are observed. From the explicit dependence of the line intensity on the dopant concentration, the new lines are attributed to the dimerization of the Er$^{3+}$-F$^-$ interstitial pairs. At higher concentrations (> 0.5 mole%), the total observed fluorescence intensity departs dramatically from a linear increase with concentration, indicative of the formation of high-order Er$^{3+}$-F$^-$ interstitial clusters. The dissociation of the dimeric clusters to single pairs occurs readily at ~1200K. The present findings help to clarify the origin of the frequently observed "cubic" site symmetry for the trivalent cation in fluorite crystals.

**Support:** MRL Program GH 33574 (National Science Foundation)
Energy Upconversion Theory of the Primary Photochemical Reaction in Plant Photosynthesis (Fong)

In this paper we suggest a basic mechanism for the utilization of light quanta in photosynthesis. Through interactions between triplets and singlets within a reaction center, light quanta absorbed in the lowest excited singlet state of the chlorophyll-a molecules are upconverted to a higher-lying triplet with subsequent conversion to a charge transfer state. It is believed that this upconversion process is important in both photosystems I and II. Steady state solutions are obtained, and the theoretical results are shown to account for a number of crucial experimental observations including the doubling (in whole cells) of in vivo fluorescence quantum yield of system II in strong light, the overall decreased quantum efficiency of in vivo fluorescence, and the recent observation by Katz and co-workers that the reaction centers consist of specific water adducts, each containing two chlorophyll molecules. Despite the apparent involvement of two excitations in the energy upconversion process, it is shown that only one quantum is needed for the transfer of one electron in the primary photochemical reaction, and that this results directly from the fact that the lifetime of the metastable low-lying triplet of the reaction center chlorophylls is anomalously lengthened as a consequence of excitonic coupling interactions between the two partner chlorophylls in the reaction center.

Support: MRL Program GH 33574 (National Science Foundation)
Growth of Single Crystals of Anhydrous Lanthanide Halides (Cox and Fong)

A consistently successful procedure for growing optically pure single crystals of the anhydrous lanthanide halides is described. It involves drying the hydrated lanthanide halide with the corresponding ammonium halide, purification by vacuum distillation, and subsequent growth by the Bridgman-Stockbarger method. All critical steps in the procedure are explained, and the relatively simple apparatus is described in detail.

Support: MRL Program GH 33574 (National Science Foundation)

Improved Theory of Activated Rate Processes: Dipolar Relaxation in Crystals, Molecular Diffusion, and Trans-Cis Isomerization (Wassam and Fong)

In this paper, we derive general quantum statistical mechanical rate expressions for activated rate processes in the harmonic approximation. The zeroth order Born-Oppenheimer states are given in terms of specified equilibrium coordinates characteristic of discrete molecular orientations or configurations. Transitions between the Born-Oppenheimer states arise from the linear interaction potential energy operator. In the high temperature (HT) limit, a simplified form of the rate expression assumes the temperature dependence

\[ W = BT^{-1/2}\exp(-E_a/RT) \]

where \( B \) and \( E_a \) are given in terms of explicit molecular parameters. At lower temperatures, a more complicated general expression must be used. The total rate in this case is a sum of five quantum scattering processes. The
overall temperature dependence is decidedly non-exponential. The validity of both the asymptotic HT and the general expression is illustrated by applying the theory in the quantitative treatment of a variety of activated rate processes including dipolar relaxation in CaF$_2$ crystals doped with trivalent cations, trans-cis isomerization of d$_2$-ethylene, and diffusion of SF$_6$ molecules in faujasite. It is shown that where the relevant molecular constants can be determined independently, the rate constants can be calculated in excellent agreement with experiment in extensive temperature ranges without any adjustable parameters.

Support: MRI Program GH 33574 (National Science Foundation)

Quantum Efficiency of Diffusion Limited Energy Transfer in La$_{1-x-y}$Ce$_x$Th$_y$PO$_4$
(Bourcet and Fong)

In this paper we present a detailed study of the concentration and temperature dependences of the quantum efficiency of energy transfer between Ce$^{3+}$ and Tb$^{3+}$ in La$_{1-x-y}$Ce$_x$Th$_y$PO$_4$. The determination of the transfer quantum efficiency in terms of the donor luminescence lifetimes is critically compared with that in terms of the donor luminescence intensities. It is shown that for the latter determination it is important to take into account any overlap in the donor and acceptor absorption spectra in the excitation wavelength region. From the exponential behavior, the concentration and thermal dependences of the donor luminescence decay, it is shown that the diffusion of donor excitation plays an important role in the energy transfer process.
Support: MRL Program GH 33574 (National Science Foundation)

**Coupling Strength in the Theory of Radiationless Transitions: \( f \rightarrow f \) and \( d \rightarrow f \) Relaxation of Rare-Earth Ions in \( \text{YAl}_2 \text{O}_3 \) and \( \text{Y}_3\text{Al}_5\text{O}_{12} \) (Lauer and Fong)**

The dependences of the radiationless relaxation rate constant on the effective mediating phonon energy, the equilibrium displacement of the adiabatic surfaces, the energy gap, and the temperature are numerically examined in terms of a generalized theoretical rate expression derived from quantum statistical theory. Special emphasis is placed on the effect of the coupling strength on the behavior of the relaxation rate process. The validity of the generalized rate expression is illustrated by its application to the fit of the temperature dependences of several \( f \rightarrow f \) and \( d \rightarrow f \) radiationless relaxation rates observed for \( \text{Er}^{3+}, \text{Eu}^{3+}, \text{Ho}^{3+}, \) and \( \text{Pr}^{3+} \) in \( \text{YAl}_2 \text{O}_3 \) and \( \text{Y}_3\text{Al}_5\text{O}_{12} \)

Support: MRL Program GH 33574 (National Science Foundation)

**Singlet-Triplet Annihilation in Chlorophyll-a (Menzel and Fong)**

In this paper, we report a novel quenching effect of the chlorophyll-a fluorescence intensity. This quenching effect is produced by the presence of a significant population of the lowest triplet state prepared by laser excitation. From the dependences of the percent quenching on sample concentration, solvent, temperature and time, the observed effect is attributed
to the diminution of the fluorescent singlet population by singlet-triplet annihilation. It is shown that migration of the donor singlet excitation plays a crucial role in the diffusion-limited transfer process.

Support: MRL Program GH 33574 (National Science Foundation)

Optical Study of the Site Symmetry Distribution in KBr:Sm$^{2+}$ (Sundberg, Lauer, Chilver, and Fong)

The 4.20K narrow line fluorescence of KBr:Sm$^{2+}$ arising from $5D_0 \rightarrow 7F_J$ transitions have been investigated in terms of Zeeman anisotropy fluorescence analysis, lifetime measurements, and Zeeman polarization determinations. There is a strong resemblance between the optical properties of the KBr:Sm$^{2+}$ system and those of the previously investigated KCl:Sm$^{2+}$ system. As in KCl:Sm$^{2+}$, the dominant site is the nearest-neighbor (n.n.) $C_2v$-$K^+$ vacancy pair. A few additional lines attributable to the second n.n. $C_4v$ pair have been found in KBr:Sm$^{2+}$. The present findings support the earlier conclusion that alkali halide crystals doped with divalent cations are usually characterized by a distribution of the first few n.n. ion defect pairs.

Support: MRL Program GH 33574 (National Science Foundation)

Publications:

"Theory of Activated Radiationless Processes: Orientation Relaxation of


"Quantum Efficiency of Diffusion Limited Energy Transfer in La_{1-x-y}Ce_xTb_yPO_4", J. C. Bourcet and F. K. Fong, to be published in J. Chem. Phys.


Talks:


Twenty-four research seminars based on recent work covering topics such as Zeeman Anisotropy Fluorescence spectroscopy, many-body energy transfer processes, energy transfer upconversion and infrared quantum counter up-conversion processes, theory of radiationless relaxation, theory of activated processes such as molecular rotation and atomic diffusion in solids, and superradiance and supernonradiance; Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan, December 15, 1972 - March 2, 1973.

"Optical Double Resonance Spectroscopy", Annual Symposium Speaker addressing the joint faculties and students, National Taiwan University, National Tsing Hua University, and Academy Sineca, January 24, 1973.


"Optical Double Resonance Spectroscopy", Department of Chemistry, Chinese University of Hong Kong, February 8, 1973.

"Relaxation Processes in Solids", Department of Physics, Chinese University of Hong Kong, February 8, 1973.
"Multiphonon Supernonradiance", Department of Physics, National Tsing Hua University, Hsinchu, Taiwan, China, March 1, 1973.


Ph.D. Theses:


Magnetization Processes in Gadolinium Iron Garnet (Friedlaender, Jones, Liedl)

The preparation and study of gadolinium iron garnet films grown epitaxially by a wet chemical process on single crystal gadolinium gallium garnet substrates is continuing. The growth processes occurring in this method of preparation have been studied by x-ray methods. One of the problems to which considerable time had to be devoted was the appearance of microscopic inclusions during the preparation of the GDIG film. Precipitation of FeOH has been observed in the nitrate solution after dilution with ethanol, prior to the application to the substrates. A marked increase in the number of inclusions has been shown to occur in films prepared from solutions in which such precipitation occurred soon after dilution. Some effort is also being made to observe the domain structure that is present in the virgin films, after cooling to room temperature. This structure consists of microscopically small domains as compared to the coarser structure obtained after cycling the sample in external fields.
Magnetic Flux Reversal in Permalloy Films (Friedlaender, Pietsch, Silva)

A modified ripple theory has been developed and wall motion threshold fields have been calculated with fields applied at arbitrary angles to the easy direction of magnetization. Measurements were made by means of the crossed-wire probe and a modified theory was derived to evaluate the film parameters by means of these measurements, taking into account ripple effects.

The model gives new insights for the evaluation of the observed data. The data fits the proposed theory consistently. Important factors requiring further investigation are brought out.

Support: None

Feasibility Study of an All Magnetic Recorder (Friedlaender, Johnson)

The purpose of the present study was to determine the feasibility of an all magnetic recording device which uses thin film technology. It became apparent early in the study that an all magnetic recording device would require the transfer of flux from one element to another. Considerable effort was expended in demonstrating experimentally that flux transfer was indeed feasible. An all magnetic logic scheme was proposed which was based on the flux transfer mechanism that has been demonstrated.

Studies were made of the disturb sensitivity of the elements in use in the present recorder. An experimental analysis of this problem
was made and a number of effects were studied by means of the Kerr magnetic-optic effect. Definite conclusions were reached and recommendations made for the improvement of the device currently in use.

**Support:** Lawrence Livermore Laboratory, Contract no. 7814309

*Magnetic Separation* (Cowen, Curtis, Friedlaender)

In this recently started work we are interested in the separation of, for instance, more paramagnetic materials from less paramagnetic materials, by means of high gradient fields. The main purpose of this work is to investigate the mechanism of operation of a high gradient field magnetic filter by carrying out carefully controlled experimentation together with analytical studies of well defined, simple systems. We expect to progress from single wire collecting systems to the more practical and much more complicated steel-wool-in-a-tube filter.

**Support:** None

**Talks:**

"Magnetische Speicher", Colloquium by F. J. Friedlaender, Krupp Forschungsinstitut, Essen, May 29, 1973


Electrical Properties of Hg\textsubscript{1-x}Mn\textsubscript{x}Te and Helicon-Excited Paramagnetic Resonance (Furdyna, Holm)

Microwave propagation studies were carried out on a series of Hg\textsubscript{1-x}Mn\textsubscript{x}Te single crystals grown in this laboratory. The composition of the samples used in this investigation was in the range $x = 0.003$ to $x = 0.100$. Microwave transmission experiments were performed at 35 GHz, in fields up to 60 kG and in the temperature range from 4.2° to 100° K. Helicon wave propagation, helicon-excited spin resonance, hole damping, and the magnetoplasma edge were observed and studied.

Electron concentration and mobility were determined from helicon transmission data. Helicon-excited spin resonance was investigated as a function of Mn\textsuperscript{++} ion concentration as well as conduction electron concentration. The latter was varied both by thermal excitation and by indium doping. It was observed that the conduction electron plasma significantly enhances the resonant interaction. The above experiment provides not only the ESR line shape, but the actual value of the dynamic magnetic susceptibility.

The observation of magnetoplasma transmission edge in cyclotron-resonance-inactive circular polarization indicates that this experiment can be exploited for the study of the static dielectric constant, which is expected to be anomalously large in a zero-gap semiconductor such as Hg\textsubscript{1-x}Mn\textsubscript{x}Te. The hole damping of helicon transmission suggests that the effect can be used to investigate the properties of holes, about which little is known in mercury chalcogenide compounds. A systematic study of the above phenomena is planned for the immediate future.

Support: National Science Foundation
Materials Research Laboratory GH33574
Precessional Motion of Plasma Oscillations in a Semiconductor Sphere and Effective Mass Determination (Furdyna and Mycielski)

Precessional self-sustained motion of plasma oscillations in a semiconductor sphere in the presence of an external magnetostatic field was predicted theoretically. It is shown that such motion can be excited by a high-frequency magnetic field transverse to the magnetostatic field. A resonance in the excitation spectrum, related to cyclotron resonance, is predicted. Since the effect is independent of carrier concentration it is suggested that this interaction can be exploited for effective mass determination in materials with high carrier concentration, where conventional cyclotron resonance fails because of plasma effects. This research was carried out jointly with Professor J. Mycielski of the Institute of Theoretical Physics, Warsaw University.

Support:  U. S. Academy of Sciences
          Polish Academy of Sciences

Publications:


Talks:


"Helicon-Excited Spin Resonance in Semiconductors with High Electron Mobility," J. K. Furdyna, presented at:


"Is it Possible to Observe Cyclotron Resonance without Plasma Shift?" J. K. Furdyna, Solid State Physics Seminar, Warsaw University, December 1, 1972.


"Excitation of EPR in $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$ by Helicon Waves," R. T. Holm and J. K. Furdyna, Conference on II-VI Semiconductor Compounds, Jaszowiec, Poland, April 1-8, 1973.


Ph.D. Thesis:

"Helicon Transmission and Helicon-Excited Paramagnetic Resonance in $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$," R. T. Holm, October 1973.
Magnetoresistance and Hall Resistivity in Very Perfect Cadmium Crystals (Richards and Gerritsen)

In view of the large effects of small amounts (order of a few ppm) of impurities on the Hall resistivity of Cd, it appears necessary to first grow Cd crystals of the highest possible purity and perfection, to establish a true reference. Growth from Cd vapor at a temperature just under the melting point (321°C) appears ideally suited for this purpose; this method has previously been used to grow the world's most perfect crystals of Mg. In effect, crystals are grown under nearly perfect annealing and purifying conditions, if the vacuum is high enough (aside from the Cd vapor itself). We have built a 5 in. I.D. split furnace for this purpose and have made several crystal growth runs simultaneously recording the vacuum pressure and the oven temperature profile. It may be necessary to further investigate the effect of different crystal growth variables upon the size of single crystals grown, in order to obtain large enough crystals for transport measurements.

Support: National Science Foundation - Materials Research Laboratory GH 33574 Al

Electrical Resistivity and Hall Resistivity of Cadmium and Cd-Alloy Crystals (Lilly and Gerritsen)

A final analysis of the large number of data obtained in this investigation has led to some more detailed conclusions that were not mentioned before.

1. The rotation of the magnetic field with respect to [0001] in the (1120) plane shows that the variation of the magnetoresistance with direction is correlated with data available in the literature on the
De Haas-Van Alphen effect and the cyclotron resonance. This is in contrast to earlier magnetoresistance data obtained in this group when the field is rotated in the (1010) plane. The present data show unambiguously that intersheet scattering does not affect temperature anomalies in the angular dependence of the magnetoresistance, under these conditions but that the main reason for these anomalies is in the anisotropy of the electron-phonon scattering.

2. The low maximum of the Hall resistivity at around 16K is clearly not due to an overall transition of $\omega \tau < 1$ to a $\omega \tau > 1$ regime. A phenomenological relation has been found between the parameters that determine the maximum and this relation contains the factor $\exp (6/kT)$, which suggests a strong phonon influence in the reason for the maximum. The results of this investigation are in publication.

Support: National Science Foundation GP 12633 Al

Zero Field Transport Properties of Cadmium and Cadmium Alloy Crystals (Sohn and Gerritsen)

Because of the relatively large effects of very small amounts of impurities on the transport properties of Cadmium the previously indicated aim of this investigation (Thermal properties) has been abolished in favor of an accurate investigation of zero field electrical resistivity.

The low temperature resistivity apparatus has been improved to provide .01% measurement precision with picovolt resolution. In the process a miniature cryostat was developed with a temperature stability of 1 part in $10^4$ over the range 4.2 - 200K.

Detailed measurements of the electrical resistivity have been taken on single crystals of pure Cd and Zn and dilute alloys of Zn and Ag in Cd in the temperature range 1.2 - 4.20K. The results offer added evidence of a fundamental scattering process in polyvalent metals which contributes a term in $\rho_i$ varying approximately as $T^3$. For the Cd samples the $T^3$ region dominates below 20K. For Zn the $T^3$ behavior is dominant
below $4.2^0\text{K}$. The alloy data show deviations from Matthiessen's Rule still exist for the most dilute alloys measured. A mechanism of phonon drag assisted impurity scattering is under consideration as a possible explanation for the $T^3$ term. It is of great interest however to determine if the $T^3$ term dissappears in the limit of a zero impurity concentration or if the effect is characteristic of a perfect lattice.

The further study of this will require purer crystals of Cd, Zn, and Mg and a greater range of alloy concentrations. For this purpose an optically heated zone refining apparatus has been put into operation, also crystals made by the vapor method will be investigated.

In relation to the above, a study of the low field magnetoresistance of pure Cd was undertaken earlier to determine possible effects of ambient magnetic fields (of the order of a few gauss) on the zero field resistivity measurements. The effects were found to be significant and a superconducting magnetic shield was devised to provide a field free environment. Although the low field magnetoresistance is of interest in itself, the interpretation is complicated by the possible presence of magnetomorphic (size effect) oscillations.

Support: National Science Foundation GP 12633 Al

Atomic Resistivity Increase Due to Rare Earth Metals in Magnesium (Hoffman, Gerritsen)

The departure, July 1, 1972, of the technician who was in charge of alloy and sample preparation has halted progress drastically. During the summer months a then BS physics graduate finished a part of the construction of an automatic data scanner, a project which was started as a undergraduate (senior) student project in the fall of 1972.

Support: National Science Foundation GP 12633 Al
Talks:

Hall Resistivity In Dilute Alloy Crystals of Cadmium; D. A. Lilly, Seminars at Kodak Physics Lab, Rochester; Physics Lab., Purdue, Oct., Nov., 1972, IBM Watson Research Lab (May '73).

Ph.D. Theses:

Multiphase Diffusion in Ternary Alloys (Sisson and Dayananda)

This research project involves an investigation of development and stability of interfaces in multiphase alloys during isothermal diffusion. The formation of planar as well as nonplanar interfaces between diffusion layers is being investigated in the Cu-Ni-Zn system at 775°C. The main objective of this study is to characterize conditions under which planar interfaces become morphologically unstable in the development of diffusion structure in ternary diffusion couples.

Experiments with diffusion couples assembled with selected α (fcc) and β (bcc) Cu-Ni-Zn alloys have shown that a transition from planar to nonplanar interfaces can occur with changes in one of the terminal compositions. Such transitions are under investigation with the following α and β alloys (composition in wt%): \( \beta_1 \) (30.5 Cu, 30.8 Ni, 48.7 Zn); \( \beta_2 \) (20.5 Cu, 24.5 Ni, 55.0 Zn); \( \alpha_1 \) (88.7 Cu, 4.1 Ni, 7.2 Zn); \( \alpha_2 \) (73.2 Cu, 8.7 Ni, 18.1 Zn); \( \alpha_3 \) (59.3 Cu, 13.3 Ni, 27.4 Zn); \( \alpha_4 \) (46.0 Cu, 17.7 Ni, 36.3 Zn). These alloys have been prepared by induction melting and their compositions correspond to approximately a constant Ni/Zn ratio. Metallographic studies of the couples \( \beta_1 \) vs. \( \alpha_1 \), \( \alpha_2 \), \( \alpha_3 \) or \( \alpha_4 \) and \( \beta_2 \) vs. \( \alpha_1 \), \( \alpha_2 \), \( \alpha_3 \) or \( \alpha_4 \) are under way. The present results indicate that the couple, \( \beta_1/Cu \), develops a nonplanar α/β interface with α needles growing into the β phase. For couples, \( \beta_1/\alpha_1 \) and \( \beta_1/\alpha_2 \), the interphase boundary is planar, and the rate of phase change becomes slower than that in \( \beta_1/Cu \) couple. The direction of phase transformation reverses for the couple \( \beta_1/\alpha_3 \), where β phase grows at the expense of α retaining a planar interface. As the rate of α to β phase change increases in the \( \beta_1/\alpha_4 \) couple, the interphase boundary
develops a nonplanar instability. Similar observations were recorded with the couple series assembled with $\beta_2$ and the $\alpha$ alloys.

A theoretical analysis of interface velocities has been developed in terms of interdiffusion fluxes of the diffusing species on either side of an interface. The test of this analysis with the experimental results requires a knowledge of the interdiffusion coefficients in both $\alpha$ and $\beta$ Cu-Zn-Ni alloys. Such data are being determined from the concentration profiles of single phase diffusion couples assembled with $\alpha$ or $\beta$ alloys. Preliminary estimates of interface velocities with the aid of calculated interdiffusion coefficients are consistent with the experimental values for all couples with planar $\alpha/\beta$ interfaces. For couples with non-planar development of the interface, it is shown that nickel which is the slowest diffusing component fails to satisfy the flux balance as required for a planar interface.

Support: U.S. AEC

Diffusion in Ag-Cd Alloys (Cheng, Dayananda, and Grace)

Diffusion in the Ag-Zn system was investigated at 600°C with both solid-solid and vapor-solid couples for the purpose of determining intrinsic and interdiffusion coefficients and vacancy wind effects in the $\alpha$ and $\beta$ phases. The solid-solid couples were assembled with disks of selected $\alpha$ alloys (16.1, 21.7, 30.1 at.pct. Zn), $\beta$ alloys (45.6, 50.7, at.pct. Zn) and a $\gamma$ alloy (59.9 at.pct. Zn) joined to disks of silver or alloy disks (9.6 at.pct. Zn). The vapor-solid couples were set up with chips of the various binary alloys ($\alpha$, $\beta$) as vapor source in contact with diffusion disks of either silver or of the selected $\alpha$ alloy. The couples were annealed for times ranging from 1 hr. to 5 days, and were studied metallographically and by electron microprobe analysis.
The diffusion data obtained from the vapor-solid couples differed little from those obtained from solid-solid couples while none was found in the vapor-solid couples.

Intrinsic diffusion coefficients, $D_{Zn}$ and $D_{Ag}$, determined experimentally for both $\alpha$ and $\beta$ alloys, were compared with those predicted by the models of Darken, Manning, and Dayananda with the aid of the tracer diffusion and thermodynamic data. Experimental values of $D_{Zn}$ were close to those predicted by the models of Darken and Manning, while the experimental $D_{Ag}$ values were higher than those determined by both models. Also, the experimental values of ratios, $D_{Zn}/D_{Ag}$, were found to be lower than those predicted by either Darken's or Manning's relations. This disagreement is considered to be due to the uncertainties in the tracer diffusivities of silver reported in literature. These uncertainties are more clearly brought out by the application of Dayananda's model.

Support: U.S. AEC

Diffusion in Ni-Al System (Robertson, Dayananda, and Grace)

Diffusion studies are being made in the Ni-Al system with solid-solid couples in order to determine intrinsic and interdiffusion coefficients in (NiAl) and (Ni$_3$Al) phases. The couples are assembled with disks of selected $\delta$ alloys (43.7, 49.1, 52.3, at.pct. Al) bonded to Ni disks and are annealed at 1000 - 1300°C for 50 - 125 hrs. All diffusion couples have been metallographically investigated and analyzed for concentration profiles by electron microprobe analysis. The evaluation of diffusion coefficients from the various profiles is currently being carried out.

Support: U.S. AEC
Diffusion in Ni-Al-Fe System (Moyer and Dayananda)

In order to investigate the transport phenomena in ternary intermetallic phases and their bonding characteristics with alloys, diffusion studies are made in the $\beta_2$ or (Ni,Fe)Al phase field of the Ni-Al-Fe system. Solid-solid couples are assembled with selected $\beta_2$ alloys for the determination of intrinsic and interdiffusion coefficients at $1000^\circ$C. The couples will be investigated by electron microprobe analysis.

Support: U.S. AEC

Publications


M.S. Thesis

Nonlinearity in Acoustic Surface Wave Propagation  (Gunshor, Lee, Schenker)

Studies continue of nonlinearities associated with the propagation of acoustic surface waves in a Si-LiNbO$_3$ configuration. (The LiNbO$_3$ crystal is Y-cut, Z propagating; an n-silicon wafer is placed close to the surface of the piezoelectric substrate.

The emphasis of experiments has been an examination of the saturation process responsible for limiting the dynamic range of devices which depend on charge bunching for nonlinearity. One new effect discovered is that an equivalent circuit representation for a surface wave convolver can contain a load-independent open-circuit source only in the linear response region of the convolver. At higher acoustic power levels the source becomes dependent on the convolver load impedance.

A theory has been developed to describe the quasi-linear operation of the Si-LiNbO$_3$ configuration as used for harmonic generation or convolution. The theory expresses the manner in which the nonlinear generation coefficient depends on the air-gap and the various semiconductor parameters. Good agreement between theory and experiment is found for signal levels below the saturation region.
Acoustic Wave Propagation and Nonlinear Interactions in Piezoelectric Layered Structures  (Gunshor, Jerabek)

This project involves the study of acoustic wave modes in layered structures consisting of CdSe films deposited by vacuum evaporation onto YX and ST α-quartz substrates. The scope of the study includes theoretical calculations of the normal acoustic modes of the structures and their associated dispersion relations, and a series of experiments to verify these calculations and to utilize nonlinear interactions of the acoustic layer waves to perform the signal processing operations of correlation and convolution. The mathematical formulation of the propagation problem is complete and is now being implemented in a computer program to solve for the normal modes and dispersion characteristics of the structures. In the laboratory some preliminary work has been done with the CdSe film evaporation process, and at the present time efforts are being made to improve the quality of the resulting films.

Support: NSF-MRL Contract No. GH 33574

Bulk Instability in GaAs  (Gunshor, Kiehl, Razouk)

Amplification properties of supercritically doped GaAs Gunn devices in microwave resonant structures are being studied experimentally and by computer simulation. These amplification properties are used to provide information concerning the internal device physics.
The dynamics of the electric field distributions in the GaAs samples are examined in computer simulations, where we are relating experimentally observed negative resistance properties to hypothesized "modes" of operation.

Support: NSF-MRL Contract No. GH 33574

Varactor Tuning of Solid State Oscillators (Gunshor, Templin)

A previously developed analytical model for a waveguide mounted Gunn effect oscillator is extended to include the presence of a voltage-dependent capacitance (semiconductor varactor and device package mounted on a second post) in a microwave oscillator. Two methods are used for theoretical calculation; the first method is based on a circuit condition of zero total reactance, the second involves a direct application of the Slater perturbation theorem. Calculations were compared to extensive experimental electronic tuning data with excellent agreement.

Support: NSF-MRL Contract No. GH 33574

Publications:


Talks:


Ph.D. Thesis:

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The principal objective of this program is to generate critical tables of standard reference data on the thermophysical properties of materials. The availability of adequate standard reference data tables is essential to the national progress, economy, and defense.

Standard reference data are generated through critical evaluation, analysis, and synthesis of the available data extracted from all sources. The procedure involves critical evaluation of the validity and accuracy of available data and related information, resolution and reconciliation of disagreements in conflicting data, correlation of data in terms of various controlling parameters (sometimes in reduced forms using the principle of corresponding states), curve fitting with theoretical or empirical equations, comparison of resulting data with theoretical predictions or with results derived from semi-theoretical relationships or from generalized empirical correlations, etc. Besides critical evaluation and analysis of the existing data, thermodynamic, kinetic, or statistical mechanical principles and semiempirical techniques are employed to fill gaps and to extrapolate existing data so that the resulting recommended reference values are internally consistent and cover as wide a range of each of the controlling parameters as possible.

Since critical evaluation, analysis, and synthesis of data are possible only when the existing data in the world literature are at hand, this program is therefore started with the search and compilation of all the existing data. The search of data is accomplished with the aid of TPRC's Scientific Documentation Division who provides comprehensive and authoritative source information on the thermophysical properties of all matter through a continuing and systematic effort in thorough search, acquisition, review, codification, classification, and organization of all the existing information in the world literature on the thermophysical properties and putting this enormous amount of information into a mechanized and computerized information storage and retrieval system (this activity is not reported here). After the existing data are compiled and organized, the second stage and major part of this program is the critical evaluation, analysis, and synthesis of the available data and the generation of critical tables of standard reference data.

As a result of this standard reference data generation program, TPRC has been officially designated both as a component of the National Standard Reference Data System—National Bureau of Standards and as an Information Analysis Center of
The properties and materials covered in the current program are:

1. Thermal conductivity--Elements, alloys, intermetallic compounds, semiconductors, nonmetallic solids, liquids, and gases.
2. Specific heat--Elements, alloys, intermetallic compounds, semiconductors, nonmetallic solids, liquids, and gases.
3. Thermal radiative properties (emittance, reflectance, absorptance, transmittance)--Elements, alloys, intermetallic compounds, semiconductors, nonmetallic solids, and coatings.
4. Thermal diffusivity--Elements, alloys, intermetallic compounds, semiconductors, and nonmetallic solids.
5. Viscosity--Liquids and gases.
6. Thermal expansion (linear and volumetric)--Elements, alloys, intermetallic compounds, semiconductors, and nonmetallic solids.
7. Electrical resistivity--Elements and alloys.

Support: Office of Standard Reference Data, National Bureau of Standards; Defense Supply Agency; Air Force Office of Scientific Research; NASA; and ASHRAE.

Publications:


Talks:

"Specialized Data Sources in the Chemical and Physical Sciences," Y. S. Touloukian, American Chemical Society Meeting, Cleveland, Ohio, May 15, 1973.


M.S. Thesis:

Electrical Properties of Nickel Oxide (Griffing, Honig, Keem, Sinha)

A series of circuits based on the use of operational amplifiers as buffers has been constructed for the study of resistivity and thermoelectric properties of single crystal specimens of NiO. As described in the last report, large specimens of high purity and high perfection were grown in an arc transfer unit and annealed in vacuo for control of stoichiometry. Plots of log $\rho$ vs. $1/T$ ($\rho$ is the resistivity, $T$, the temperature) were linear; between 800 and 520 K an activation energy of 0.1 ev was observed, while below the Néel point the activation energy was 0.6 ev. At approximately 130 K, nonlinearities were encountered which could be suppressed by reducing the current; the I-V characteristics of this region are being investigated. The Seebeck coefficient of NiO was found to be nearly independent of temperature between 700 and 275 K; in particular, the onset of magnetic order is not reflected in these measurements.

Further studies, inclusive of photoconductivity measurements, are contemplated in attempts to elucidate the band structure of this material.

Support: NSF GP 29221
ESCA Study of the Band Structure of Oxides (Honig, Kuwamoto, Wahnsiedler)

A complete study has been made of the band structure of NbO by use of x-ray photoelectron spectroscopy for binding energies in the range 0 to 700 ev. All of the bands have been identified and correlated with atomic levels. The Fermi level is intercepted by several broad bands, which explains the highly metallic characteristics of this compound. The results will be used in assessing the theoretical calculations of the band structure described below.

Support: NSF GP 29221

Band Structure Calculations of NbO (Honig, Wahnsiedler)

Using the APW technique in conjunction with atomic wave functions provided by Liberman, attempts are under way to calculate the band structure of NbO at points of high symmetry in the central Brillouin zone. These results are then to be used as input parameters to the Slater-Koster adaptation of the tight-binding scheme for a complete band structure determination.

Two check runs using published results by Burdick for Cu and by Ern & Zwitendick for TiC have been performed to determine whether all of the programs function correctly. Having established that this is the case, final calculations for the NbO structure are being initiated.

Support: NSF GP 29221
Electrical Properties of Sc-Doped Ti$_2$O$_3$ (Chandrashekhar, Honig, Jayaraman, Van Zandt)

Measurements have been completed on the higher order electrical transition in $(\text{Sc}_x\text{Ti}_{1-x})_2\text{O}_3$ with $0 \leq x \leq 0.05$. In contrast to the $(\text{V}_x\text{Ti}_{1-x})_2\text{O}_3$ system, the semiconducting phase is not suppressed on addition of Sc. As with the V-doped system, the transition temperature range is very little altered on doping with Sc. A theory is being developed in attempts to account for the difference in properties between the Sc-doped and V-doped Ti$_2$O$_3$ systems.

Support: NSF-MRL GH 33574

Electrical Properties of the V$_2$O$_3$-Cr$_2$O$_3$ System (Chandrashekhar, Honig, Jayaraman, Kuwamoto, Sinha)

An extensive series of measurements has been completed on the structure, heat capacity, resistivity, and Seebeck coefficient of pure single crystals of $(\text{Cr}_x\text{V}_{1-x})_2\text{O}_3$ with $0 \leq x \leq 0.015$. In agreement with earlier published results, a first order metal-insulator transition, accompanied by an enthalpy change of ca. 700 cal/mole V$_2$O$_3$ is encountered at 160 K. However, the higher temperature transition near 350 K was found to be very dependent on the thermal history of the sample, and was accompanied by enthalpy changes of only 60 cal/mole V$_2$O$_3$ or less. Furthermore, the higher temperature anomaly was characterized by the presence of two crystallographic phases of rhombohedral symmetry, differing only slightly in lattice cell parameters. Beyond 500 K another, previously undetected metallic range was encountered, which corresponds to a monophasic region.

These observations call in question the generally accepted hypothesis that the higher temperature anomaly represents an example of a Mott
transition. Rather, we postulate that the anomaly is a manifestation of electron scattering and trapping in boundary regions of the two coexisting phases; the anomaly is thus extrinsic to the system and disappears in the temperature ranges where the only single phases are encountered.

**Support:** NSF-MRL. GH 33574

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**Electrical Properties of the (Ti\(_{1-x}\))\(_2\)O\(_3\) System** (Chandrashekhar, Honig, Jayaraman, Van Zandt)

Measurements similar to those described for the (Cr\(_{1-x}\))\(_2\)O\(_3\) system have been completed. The effect of adding Ti to V\(_2\)O\(_3\) is to reduce and ultimately suppress the low temperature transition in V\(_2\)O\(_3\) and to render the system more metallic.

**Support:** NSF-MRL. GH 33574

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**Tunnelling Experiments in V-doped Ti\(_2\)O\(_3\)** (Eklund, Van Zandt)

Equipment has been constructed for the measurement of I vs. V curves and of their first and second derivatives for use in tunnelling experiments. Data have now been obtained for V-doped Ti\(_2\)O\(_3\) in the cryogenic temperature range, using either In or Pb as contacts. A change in resistivity of the junction was encountered at a bias of ±1.5 meV. This is interpreted as arising from the opening up of a new channel involving inelastic scattering of electrons from impurities or vanadium whose levels are split in the host matrix which furnishes an inversion layer near the junction. Experiments are continuing on the effects of varying the
temperature and of imposing magnetic fields. As far as is known, this is the first experimentation of its type on an oxide system.

Support: NSF GP 29221

Publications:


Talks:
"Metallic Conduction in Metal Oxides", presented by J. M. Honig to the Department of Chemistry, University of Groningen, Netherlands, September 1972.

"Metallic Conduction in Non-Metals", presented by J. M. Honig at the NATO Sponsored Advanced Study Institute, Belgirate, Italy, September 12, 1972.


"Electrical Properties of Metallic Oxides", presented by J. M. Honig to the Department of Materials Sciences, Northwestern University, November 21, 1972.

"Metallic Conductivity of Non-Metals", presented by J. M. Honig to the Corning Research Laboratory, Corning, New York, December 8, 1972.


Ph.D. Thesis:
"Electrical and Raman Studies of Pure and V-doped Ti$_2$O$_3$, S. H. Shin,
December 1972.
Central Crystal Growth Facility

Staff Member: J. M. Honig
Professor of Chemistry

Research Associates: H. R. Harrison
G. V. Chandrashekhar

Research Assistants: G. Yuochunas
P. Eklund
J. Keem

Crystal Growth
(a) Metal Oxides (Chandrashekhar, Yuochunas, Eklund, and Keem)

Using either a resistance heated furnace with an appropriate crucible or a crucible-less tri-arc melter or an arc-transfer furnace, the following types of single crystals were grown: pure, Sc- and V-doped Ti$_2$O$_3$, pure and Cr- or Al-doped V$_2$O$_3$, NiO, NbO, SmTiO$_3$, KTaO$_3$, LaTiO$_3$, and GdTiO$_3$. These crystals have been supplied to various researchers in the Departments of Chemistry or Physics and the School of Electrical Engineering at Purdue; also, to individuals at the Massachusetts Institute of Technology, Yeshiva University, Northwestern University, Case Western Reserve University, Ford Motor Company, and to researchers residing in France, Japan, and India.

(b) Alkali Halides (Harrison)

Using a moving furnace (Pt-Rh resistance wound) Bridgman apparatus, a continuing series of doped alkali halide crystals are being grown for members of the Department of Physics.

(c) Metals (Harrison)

Using a rf induction Bridgman apparatus, several series of crystals are being (or have been) grown for members of the School of Materials Engineering: (i) Copper-iron single crystals. (ii) Niobium samples annealed and oxygen-doped. (iii) Very uniform polycrystalline alloy rods of iron-nickel-titanium, iron-nickel-cobalt-carbon, and iron-nickel-carbon are being
produced in a vacuum melter. (iv) Iron-nickel-titanium single crystals.
In addition to crystal growth, some experimental analyses of the iron-nickel-
titanium single crystals were performed with the electron microprobe and
scanning electron microscope. (v) In addition, an aluminum single crystal
was grown for a member of the Department of Physics.
(d) Semiconductors (Chandrashekhar, Harrison, and Yuochunas)

Using an induction-heated Czochralsky apparatus, several attempts
were made to grow large GaSb crystals. So far only polycrystalline samples
with large grains have been obtained.

New Equipment Constructed
(i) (Harrison)

A new moving furnace (Pt-Rh resistance wound) Bridgman apparatus
was constructed and put into operation. A portable vacuum system to be used
with this and other various crystal growing and annealing facilities was also
constructed. The rf induction unit used with most of the Bridgman growth
has been considerably improved.
(ii) (Harrison, Chandrashekhar, and Yuochunas)

A resistance heated Centorr furnace has been modified to grow or anneal
crystals either in vacuum or in varying atmospheres. Using this set-up two
unsuccessful attempts were made to anneal tantalum foils in vacuum at ≈2200°C
for the Department of Physics, but attempts in a gettered argon atmosphere
were successful.
(iii) (Harrison)

A vacuum melter for the preparation of very uniform metal alloy rods
has been repaired. Some of the rods are subsequently grown into single
crystals in the rf induction Bridgman apparatus, and some are used in poly-
crystalline form directly by members of the School of Materials Engineering.
(iv) (Harrison)

An acid saw for low stress cutting of pure metal crystals has been
repaired.
Equipment Under Construction

(i) (Chandrashekhar)
A few unsuccessful attempts have been made to grow oxide single crystals by chemical vapor transport techniques. Attempts are being made to improve the temperature profile in the furnace employed and to optimize the other parameters involved.

(ii) (Harrison, Chandrashekhar, and Yuochunas)
A commercial horizontal zone leveler-zone refiner has recently been purchased. Growth of single crystals of gallium arsenide and cadmium (for members of the Department of Physics) will be undertaken shortly.

(iii) A commercial low speed diamond wheel saw for low stress cutting of metal crystals has just been purchased.

Miscellaneous Work
Crystal cutting services have been provided using diamond, wire and acid saws.

Support: ARPA-IDL
NSF-MRL, GH 33574

Publications:
Ordering of Molecules in Solid CO and N₂ (James and Hall)

Unlike H₂ and HD, the N₂ and CO crystals are not "quantum crystals," though quantum effects are important in them. They offer an appropriate field for the study of anharmonic librations in cases where classical mechanical ideas are more relevant than they are in ortho-H₂. CO is particularly interesting because its center of mass (like that of HD) does not coincide with its geometric center, a fact that has been ignored in all earlier treatments of the crystal. CO is also interesting because of the end-for-end disorder indicated by its residual entropy at low temperatures, which complicates the dynamics of the crystal. An attempt is being made to attain a better understanding of the P₂₁₃ structure and the dynamic behavior of CO and N₂, using a model that includes quadrupole-quadrupole and atom-to-atom van der Waals coupling of the molecules, retaining quartic terms in the expansions of the interactions about the equilibrium configuration of the crystal, and employing the quasiharmonic approximation.

Support: NSF Grant GP-19434
Mechanical, Thermophysical, Electrical, and Magnetic Properties of Geological Substances, Nuclear Blast Effects on Rock Properties and on Earth Media, and Rapid Excavation and Tunneling Technology (Judd, DeWitt, West, Touloukian, Desai, Chung, Kalkani, Navarro, Von Frese, and Egan)

The primary objective of this project is to establish data banks in the Rock Properties Information Center (RPIC), which is a national data center of rock properties, nuclear blast effects on rock properties and on earth media, and of rapid excavation and tunneling technology. This project also has an experimental program for the measurement of the properties of rocks.

The major activities of the current program are summarized below.

1. The generation of data tables for the mechanical, thermophysical, electrical, and magnetic properties of rocks and minerals.

   The data bank includes results of both in-situ and laboratory tests. Particularly important is the inclusion of sufficient sample characterization and test conditions to permit data evaluation and correlation and the preparation of reference data tables. Data are compiled for the following properties:

   a. Mechanical properties

      Compressive strength (unconfined and triaxial), shear strength, tensile strength, compressive deformability, tensile deformability, cyclic deformation, Young's
modulus, modulus of deformation, modulus of rigidity, modulus of rupture,
Poisson's ratio, impact toughness, hardness (abrasive and scleroscope), damping
capacity, etc.

b. Thermophysical properties

Thermal conductivity, thermal diffusivity, thermal expansion (linear and
volumetric), density, specific heat, thermal radiative properties, etc.

c. Electrical and magnetic properties

Electrical resistivity (conductivity), dielectric constant, dielectric loss,
magnetic permeability, remanent magnetization, etc.

2. The organization and codification of unclassified literature on nuclear/high explosive
blast effects on rock properties and on the geological blast area.

The objective is to collect all information relating to the shock effects on
various rock properties; transient ground motion studies which include shock pres-
sure and stress, transient strain, particle velocity and acceleration, particle
displacement, and seismic velocities; electromagnetic pulse effects; and the geologi-
cal situation at the shot and at the instrument points and in between these two points.
The recorded information also includes operation and shot name, elevation and depth
of burst, detonation coordinates, date and time, and type of burst and yield.

3. The organization and codification of the literature on rapid excavation and tunneling.

The objective is to collect all information on types of tunnel, geometry and
size of excavation, types of excavation techniques, energy input, rates of excavation
and cost, equipment characteristics and manufacturers, thrust and torque of the
machines, cutting head temperatures, methods of material handling, the organiza-
tions performing and funding the excavation, and all relevant geological data.

4. The companion experimental program.

The objective is to measure the thermal conductivity, thermal diffusivity, and
related parameters on petrographically characterized rocks and to correlate their
thermal and mechanical properties.

Support: National Science Foundation (NSF-RANN)
The original objective of the research has been to reconstruct a three-dimensional image of an object from an acoustic hologram. Preliminary investigation has produced evidence that no general operation on the hologram itself will yield a useful three-dimensional image (although two-dimensional reconstructions are feasible and have proved to be useful), but that the hologram can be used to obtain the field pattern of an insonified object. The work has, therefore, been concentrated on the three-dimensional reconstruction of an object from its field pattern.

The computer has been used to determine the fields in one plane from those in another plane. By application of the algorithm over a bounded object space, it has been determined that features occur in the patterns which can be used to uniquely describe the object which created the initial insonified field. Simulated objects have been located in space from a distant field pattern, and progress is being made on the description of these objects.

An experimental apparatus for acoustic holography is under construction. The apparatus will be used to generate a hologram of a test object for use in the present investigation, and will provide a real time imaging capability for anticipated future research.
Support: NSF/MRL GH 33574

M. S. Theses:

"Computer Reconstruction of Objects from Holographically Recorded Sound Fields,"

Specific Heat of Niobium in the Mixed State (Keesom and Okaz)

Type II superconductors, e.g. niobium, can be brought in the mixed state by applying a magnetic field. In this state the sample is threaded by a triangular lattice of vortices, surrounded by superconductive material. The contribution to the specific heat of the superconductive material is small as compared to the contributions of the material inside the vortices. This latter material behaves as if it is in the normal state and contributes a term linear in temperature to the specific heat. Existing theory of the mixed state, however, predicts that at sufficient low temperature, probably for niobium in the order of 0.03 K, that the specific heat will become exponentially dependent on the temperature.

We are trying to cool a niobium sample down to this low temperature so that the specific heat can be measured. We encounter experimental difficulties to cool the sample below 0.07 K, although the surrounding of the sample is kept at 0.02 K. Probably minute vibrations of the sample have to be eliminated, as an extraneous heat input of one erg per minute has been measured. In addition the thermal contact between dissimilar material will have to be improved.

Support: National Science Foundation GH34403

Specific Heat of Transition Metal Oxides (Keesom, Wenger and Honig)

After we finished the investigation on Specific heat of V doped Ti₂O₃ (see previous progress report) we have started the investigation of V₂O₃ doped with metal ions.

The vanadium sesquioxide V₂O₃ is an antiferromagnet at low temperature; it is, however, unstable against a cooling and heating cycle which make it difficult to use single crystals for low temperature investigations. Adding
several percent of \( \text{Cr}_2\text{O}_3 \) to \( \text{V}_2\text{O}_3 \) overcomes this difficulty.

Below 1 K the dominant contribution to the specific heat comes from the nuclei of the vanadium ions, which energy levels are split due to the local magnetic field of this antiferromagnetic material. This effect has been investigated elsewhere, but with very small crystals to overcome the unstability problem, however, this leads to uncertainty in the result due to the extra specific heat of the container. In comparison with nuclear resonance data the specific heat result appear about 20% to low. We have started to measure the specific heat of several large chromium doped \( \text{V}_2\text{O}_3 \) crystals and our preliminary results indicate better agreement with the nuclear resonance data.

Support: National Science Foundation GH34731

Interfacing Specific Heat Measurements with an IBM Card Puncher (Keesom and Hoo)

In measuring specific heat the temperature of a sample has to be followed as a function of time at the moment this is done by following the resistance of a germanium thermometer on a stripchart recorder. After the measurements are done the data have to be transferred to IBM cards, and sent to a computer. This involves one or two days.

It appears of interest to have data punched directly on cards, during the measurements, so that results can be obtained from the computer without delay allowing the measurements of additional data. Also human errors may be avoided.

We have build an interfacer between our electrical measuring equipment and an IBM card puncher. Nearly all the components of this interfacer have been checked now and work as expected.

Support: National Science Foundation GH34403

Publications:


Talk:

Radiation Annealing of Bombardment - Produced Defects in n-Type Silicon
(Klontz and Ports)

Continuation of studies of bombardment damage and radiation annealing has been carried out at temperatures up to 52K. A small amount of permanent damage is introduced by the 1MeV electron beam but it is still several orders of magnitude smaller than damage produced above 60K. After damage is produced at 52K, partial radiation "annealing" of the damage is observed using 350 keV electrons at temperatures of 36K and 44K. This "annealing" is not permanent and over a period of several days the electrical properties of the samples slowly drift back to the values they had after the damaging bombardment. No effect is observed if the 350 keV beam is used at 52K. The results do not depend on the oxygen content of the material since about the same numbers of defects are produced and annealed in both float zone and pulled material. These defects are entirely different in their behavior than are those formed at higher temperatures and it is probable that the "annealing" is not a change in the basic structure of the defect but rather a long time trapping effect.

Support: National Science Foundation - Materials Research Laboratory GH 33574.

Ph.D. Thesis:
"Defects Induced by Electron Irradiation in p-Type Germanium at Low Temperatures" Richard A. Matula, August 1973.
The Hg-Se-S System and its Geologic Implications (Boctor and Kullerud)

Objective: To understand the physical and chemical conditions under which the sulfides and sulfoselenides of mercury are formed in nature.

Approach: A systematic investigation of the phase relations in the system Hg-Se-S; a study of the kinetics of the cinnabar → metacinnabar inversion; a mineralogical and geochemical study of pertinent mercury ores and the application of the experimental investigations to mineral assemblages in nature.

Progress:

1. The Hg-Se-S system:

We continued our investigation of the phase relations in the system Hg-S-Se between 500°C and 200°C and started an investigation of the relations on the S-Se rich side of the system between 500 and 750°C. The results obtained to date are as follows:

a. The liquidus relations on the S-Se join were determined by the "appearance of phase" method through visual and optical examination of the quenched experimental products. An attempt to determine the liquidus temperatures by dilatometric methods was not successful. It was difficult to prepare samples of the appropriate shape and size required for the dilatometer because of the low hardness of S-Se alloys. Selenium was found to have a significant effect in lowering the temperature of polymerization
of pure sulfur. Thus the addition of 10% Se in solid solution lowered the polymerization temperature from 160°C ± 1°C to 118 ± 3°C. This value is in agreement with the threshold of polymerization of $S_{0.9}Se_{0.1}$ determined by Ward and Myers (1968) using Raman spectroscopy and differential scanning calorimetry.

b. He Hg-S join:

The melting of HgS was investigated using the "appearance of phase" method and differential thermal analysis. A maximum melting of 572 ± 3°C was reported by Potter and Barnes (1972) and Potter (1973) for this compound. The temperatures at which liquid HgS coexists with liquid sulfur and liquid mercury as given by these authors are 475 ± 4°C and 485 ± 2°C respectively. These results contradict those given by Kullerud (1965) who reported a melting temperature of 825 ± 1°C for stoichiometric HgS and temperatures of 795°C and 805°C for the coexistence of liquid HgS with liquid S and liquid Hg respectively. A reinvestigation of the temperature of melting of HgS and the temperatures of coexistence of liquid HgS with liquid S and Hg was undertaken using 2 different differential thermal analysis apparatus at Purdue University and at the United States Geological Survey Laboratories at Washington, D.C. The results obtained agree with those previously reported by Kullerud (1965). Confirmation of these results was also obtained by monitoring the melting visually in a vertical furnace in which the temperature was controlled by ± 2°C. Potter (personal communication) determined the "melting" by monitoring the change in resistivity of powdered HgS as a function of temperature. The temperature of sublimation of HgS is 580°C. Apparently the temperature reported by Potter and Barnes (1972) is not related to melting but instead corresponds to the temperature of
sublimation. These authors did not extend their investigations to temperatures above 600°C. Currently an investigation is in progress of the limits of nonstoichiometry in HgS as a function of temperature.

c. The Hg-Se join:

Our investigation of the low temperature relations in the Hg-Se system showed considerable deviation from stoichiometry in HgSe. This was overlooked by Strauss and Farrell (1963) who studied the phase relations in this system. Between 550°C and 450°C mercury selenide has a composition ranging from 49.0 ± 0.1 at.% Hg to 51.1 ± 0.1 wt.% Hg. These compositional limits were observed in mercury selenide synthesized directly from the elements as well as in the products resulting from heating stoichiometric HgSe together with appropriate amounts of either Hg or Se. The compositional limits for mercury selenide at temperatures above 550°C and below 450°C are being investigated. We are also investigating the mercury rich portion of the Hg-Se system which has as yet not been systematically explored.

d. HgS-HgSe solid solution series:

The HgS-HgSe solid solution series was studied at temperatures between 750 and 200°C. Stoichiometric HgS and HgSe were used as starting material. A continuous solid solution was found to exist over the temperature range from 750°C to 400°C. Compositions with small amounts of HgSe in solid solution showed on quenching the cinnabar structure. Increasing percentage of HgSe in solid solution stabilizes the sphalerite type structure of metacinnabar in the quenched products. The compositional limits between the two types of structures as a function of temperatures are as follows:
Temperature | Cinnabar type structure | Sphalerite type structure
---|---|---
750°C | <10 mole % HgSe | >15 mole % HgSe
600°C | <12 mole % HgSe | >18 mole % HgSe
500°C | <13 mole % HgSe | >23 mole % HgSe
400°C | <14.5 mole % HgSe | >26 mole % HgSe

Compositions lying between these compositional limits showed upon quenching one phase with the sphalerite type structure. This phase however partially inverted to the cinnabar type structure when left at room temperature.

Below 345°C the HgS-HgSe solid solution can no longer remain complete. Measurements of the solubility of HgS in HgSe at 300°C showed a limit of solid solution at HgSe$_{30}$HgS$_{70}$. At 200°C this solubility has decreased dramatically to HgSe$_{60}$HgS$_{40}$. Compositions lying beyond these limits on the HgS rich side of the series on quenching constituted of two distinct phases. One of these phases had the sphalerite type structure with partial inversion to cinnabar whereas the other phase showed the cinnabar type structure. Homogeneous products were not obtained at these temperatures even after heating for 4 months.

Differential thermal analysis experiments performed on compositions producing the cinnabar type structure showed that Se plays a significant role in lowering the temperature of the cinnabar$\Rightarrow$metacinnabar inversion. Two mole % HgSe in solid solution in stoichiometric HgS lowers the inversion temperature from 345 ± 3°C to 325 ± 5°C. This effect increased with increasing Se content and the inversion temperature is lowered to 248 ± 3°C when the amount of HgSe in solid solution is increased to 10 mole %. HgS with 20 mole % HgSe in solid solution which showed partial inversion to cinnabar when left at room temperature after quenching from 500°C gave an inversion temperature of 121 ± 5°C upon heating.
The ternary phase relations involving the HgS-HgSe solid solution in the Hg-S-Se system are being investigated at 300 and 200°C as well as above 500°C.

2. The metacinnabar-cinnabar relations

A kinetic study of the metacinnabar-cinnabar inversion is in progress. Homogeneous HgS doped with small amounts of ZnS, FeS and HgSe in solid solution was used in this study. To ensure the homogeneity of the starting material, all compositions were synthesized at 835°C which is above the melting point of pure HgS. We found by differential thermal analysis that our doped HgS also melts below this temperature. We further annealed the homogenized compositions at 600°C and then quenched them to room temperature. In our experiments we used the compositions that upon quenching yielded metacinnabar which showed no sign of inversion either optically or in X-ray diffraction patterns. The annealing periods of these compositions at 835 and 600°C as well as their particle sizes were kept constant. An isothermal rate study was conducted at 95 ± 2°C, the temperature at which metacinnabar and cinnabar coexist in present day hot springs. The transformation is being studied by monitoring the change in X-ray intensities of the 002 reflection of metacinnabar and the 1012 reflection of cinnabar. These two reflections were found to have nearly identical intensities relative to each other at the operating conditions of 25 KV, 10 MA, CuKa radiation and using a graphite monochemator under constant diffractometer setting. A series of synthetic mixtures of cinnabar and metacinnabar were prepared and the intensities of the 1012 and 002 reflections were monitored under the instrumental conditions outlined above. Exactly 30 mg. of material was used in preparing the X-ray smear mounts and the area on which the powder was dispersed was also kept
constant. A polynomial regression computer program was used in refining the data and the change in the intensities expressed as I cinnabar/I cinnabar + I metacinnabar was plotted as a function of wt% cinnabar in the mixtures. The plotted curve was used to measure the fraction transformed in our experiments. The results of the kinetic study to date are as follows:

a. For HgS doped with 0.3 mole % ZnS a maximum transformation of 53% was obtained after annealing for 396 hours. An incubation period of 48 hours was observed at the beginning of the transformation followed by a progressive increase in the rate of transformation. After 310 hours when total transformation was 47% the rate of transformation decreased markedly and substantial increase in the rate was not observed with increasing times. HgS with 0.2 mole % Zn in solid solution showed partial transformation on quenching from 600°C to room temperature. Compositions with impurity contents between 0.3 and 0.2 mole % ZnS are under investigation.

b. HgS with 10 mole % HgSe in solid solution showed only 5% transformation after annealing at 95°C for 25 hours and no increase in the fraction transformed was observed upon annealing for 100 hours. HgS with 7 mole % HgSe in solid solution showed incipient inversion upon quenching from 600°C to room temperature.

c. HgS with 0.5 Fe in solid solution showed a maximum transformation of 9.5% after annealing at 95°C for 74 hours and this value remained constant when the annealing time was increased to 150 hours. HgS with 0.3% FeS in solid solution partially transformed on quenching from 600°C.

In none of our experiments were we able to obtain complete transformation of metacinnabar to cinnabar, not even in those experiments in which metacinnabar showed partial transformation at room temperature. This phenomenon was observed as well in a study of the occurrence of the two polymorphs in natural mineral assemblages. In an
attempt to explain this behavior, we performed electron microprobe analyses of the
doped HgS before and after annealing at 950C. Our results must be considered
semiquantitative because of the fine grained nature of the material used in our experi-
ments. However we noted that uninverted metacinnabar displays uniform distribution
of impurities whereas partially inverted metacinnabar is inhomogeneous. A tendency
of increase in impurity content at the interface between metacinnabar and cinnabar
is evident in inverted grains. The same feature was noticed in natural cinnabar and
metacinnabar grains in which we were able to quantitatively determine the spatial
distribution of impurities. Concentration of impurities at the interface between the
two polymorphs apparently prohibits further nucleation of cinnabar.

We are currently studying the rate of transformation in additional compositions
at 950C. We are also investigating the compositions previously studied at temperatures
both below and above 950C.

Mineralogical and geochemical studies:

1. The natural analog of the HgS-HgSe series at Lucky Boy Mine, Marysvale,
Utah were studied mineralogically and analyzed by the microprobe. Synthetic members
of the HgS-HgSe series were used as standards. The sulfoselenide minerals studied
ranged in composition from HgS$_{77}$-$HgSe_{23}$ to HgS$_{13}$-$HgSe_{87}$. The samples were generally
uniform in composition although a few samples displayed zoning. The compositional
inhomogeneity of the zoned samples is of large magnitude and ranges between HgS$_{34.5}$-$HgSe_{65.5}$ and HgS$_{76.7}$-$HgSe_{23.3}$. The concentrations of Fe and Zn in the sulfoselenides
are (0.01%. Apparently Se is responsible for the stabilization of the sphalerite type
structure in this series. Minor amounts of sphalerite and pyrite occur in this ore.
The sphalerite contains up to 11 wt.% Hg in solid solution which is the highest Hg content reported for this mineral.

2. Microprobe analysis of mercury ores from Mount Diablo and New Idria Mines, California showed that the concentration of Zn and Se in metacinnabar is 0.01%. Fe seems to be the major impurity in the metacinnabar of both mines ranging from 1.0 to 2.2 wt.% with an average of 1.3 wt.% at Mount Diablo and from 0.7 to 2.8 wt.% with an average of 1.6 at New Idria. Microprobe traverses show that the interface between the cinnabar and metacinnabar is enriched in Fe. The iron content at the interface is up to 0.6 wt.% higher than the inner zones of the grains. Cinnabar has an iron content ranging between 0.1 and 0.4%.

3. Microprobe analysis of mercury ores from the Senator Mine, Nevada shows that the metacinnabar from this mine is remarkably enriched in Zn and Fe; up to 4 wt.% Zn and 2.5 wt.% iron in solid solution. The concentration of Se is <0.01. The metacinnabar is associated with barite. The occurrence of both sulfides and sulfates in ore deposits was subject to different interpretations by geologists. The coexistence of these two species was attributed by some investigators to the maintainence of a delicate balance between the oxygen and sulfur fugacities in the mineralizing solutions, to the oxidation of sulfide to sulfate or to the reduction of sulfate to sulfide. In our case the metacinnabar appears to have been deposited later than the sulfate which will imply a reduction of sulfate. Confirmation of this conclusion awaits the results of a sulfur isotope study of both barite and metacinnabar samples.

Support: ARPA continuation, NSF-MRL program at Purdue Grant GH33574

Publications: Two in preparation
Talks:


PhD Thesis:

Structural Effects of Bi in Amorphous Si Films (Braun, Grimm, Neudeck, and Liedl)

The structural arrangement and strains of the silicon tetrahedra have a direct effect on the electrical properties. Considerable controversy exists in the literature over the structure of covalent bonded amorphous solids such as silicon. This controversy evolves from a number of investigations deducing a structural model from either X-ray data or electrical properties data. This study will attempt to correlate the two types of information along with fabrication parameters and annealing.

Two cathodes, one of sintered pure silicon powder and one with sintered 22.5 wt. % Bi-Si, were obtained for the sputtering fabrication of the films. A series of sputtering runs were made for each cathode to characterize the influence of fabrication parameters such as RF power, argon pressure, and substrate temperature on the film formation.

The resistivity of the as-fabricated films were strongly dependent on fabrication parameters such as deposition rate, substrate temperature, and presence of alloying element. As fabricated pure Si films exhibited a range in resistivities from $4.2 \times 10^4$ to $1.4 \times 10^5$ ohm-cm for deposition rates between 4 and 8 Å/sec and substrate temperatures between $-196^\circ C$ and $110^\circ C$. After annealing at $500^\circ C$ for 30 minutes, the room temperature resistivity of all silicon films was approximately $5 \times 10^6$ ohm-cm and was independent of any temperature cycle to less than $500^\circ C$. Resistivity versus reciprocal temperature data indicates a single activation energy for conduction of 0.48 eV near ambient temperature after annealing.

The Si-Bi films as-fabricated resistivities varied between $3.7 \times 10^3$ and $5.5 \times 10^4$ ohm-cm and after annealing to $500^\circ C$ for 30 minutes varied between $3 \times 10^5$ and $3.5 \times 10^6$ ohm-cm. A variation in Bi content could not be directly
correlated with the resistivity variation and indicates possible fabrication effects remain. However, resistivity between ambient and 500°C remain unchanged upon cycling of temperature which indicates thermal stability of the properties within this temperature range. The activation energy for conduction was found to be 0.35 eV after annealing and independent of fabrication variations.

The diffuse X-ray scattering was measured for both a pure Si and a Si-Bi film as-fabricated. Both patterns show the expected intensity maxima corresponding to nearest neighbor spacing in silicon tetrahedra and another corresponding to second and third nearest neighbor in coupled tetrahedra. However, the diffuse maxima for the Si-Bi films are sharper than those of pure Si indicating less disorder in both atomic bond lengths and angles. This result is the opposite of the expected result and is being studied further.

Support: NSF GH33574

Anodic Oxidation of Reactively Sputtered Tantalum Oxynitride Thin Films (Englund and Liedl)

Historically, tantalum film technology has been of prime importance in microcircuit technology, both in the production of capacitors and resistors. Previous studies involved essentially pure tantalum (in bulk or as a film) or essentially binary films where the amount of O or N in the film is varied. Presently, the design of RC hybrid circuits calls for a match between the temperature coefficient of capacitance in the capacitor film and the temperature coefficient of resistance in the thin film resistors to assure stability over a wide range of temperature without the use of thermistors. Because these resistors are precision tuned to value by anodization techniques, it is important to study the anodization of these tantalum oxynitride films. This work involves the study of the anodization of tantalum oxynitride films with a constant TCR of -220 ppm, and various ratios of oxygen to nitrogen. The films were anodized at constant current and the resulting properties, such as anodization constants and current efficiency of the anodic oxides, were compared to the structure and composition of the metal films.

The films were reactively D.C. sputtered in an Ar-O-N atmosphere onto an oxidized thin layer of β-Ta on glass slides. Reactive gases were N₂O and O/N ratios of 0.5, 1.0, 1.5, and 4.0. Anodization was carried out at constant current densities of 0.1, 1.0, and 10 mA/cm² in a 0.01 percent citric acid solution.
The reactive gas content of the sputtered films varied from an O/N ratio of 0.482 to 2.09 for the reactive gases employed. For O/N ratio less than 0.65, the predominant phase was TaN, changing to TaN for ratios up to 0.9 and bcc Ta for a ratio of 2.09.

The anodization parameters $Y'$ and $K'$, the reduction of film thickness and the increase in oxide thickness per coulomb of charge passed through the cell respectively, exhibited discontinuities with O/N ratios that correlates with the nitride phase changes. Also, films with TaN phase did not produce a protective oxide and consequently are not suitable for resistor material. The oxide phase produced in the presence of TaN or $\text{Ta}_2\text{N}$ is apparently a complex of $\text{TaO}_{x\_y}$ which needs to be studied further.

Support: Western Electric Company

Publications:

Talks:

M.S. Theses:
Trace Element Contents of Materials (Binz, Ikramuddin, Rey and Lipschutz)

The overall aim of this study is to develop analytical methods for the determination of a large number of trace elements of differing volatility in a single 0.5 gram sample and to use these methods to investigate "primitive" meteorites - i.e. to study the condensation and evolutionary processes existing in the early solar system. The elemental abundance patterns and distribution of statistically-significant inter-element correlations and anti-correlations in carbonaceous and unequilibrated ordinary chondrites have been discussed in papers c and d on the attached list. Our results indicate pronounced differences in the formation conditions of primitive chondrites. The carbonaceous chondrites seem to have resulted from the simple mixing of two components differing in thermal history. The unequilibrated ordinary chondrites seem to have resulted from a metal-silicate fractionation in the solar nebula followed by a thermal fractionation occurring either during condensation of solid material from the nebula or, following condensation, in the meteorites' parent body or bodies.

We have used similar procedures to determine As, Au, Bi, Cd, Co, Cu, Ga, In, Sb, Se, Te, Tl and Zn in another group of primitive meteorites, the enstatite chondrites. We have determined the patterns of correlations and anti-correlations involving these 13 elements and literature data for 21 additional elements and are currently engaged in writing up the results. We are also completing determination of these 13 elements in the remaining known unequilibrated ordinary chondrites to clarify certain trends noted in
our earlier survey.

We have also used atomic absorption spectrometry to provide analytical data in support of the research activities of the groups of Professors Honig, Porile and Vest.

**Support:** NASA grant 15-005-140, PRF, NSF-MRL

**Shock-Induced Effects in Solids** (Jain and Lipschutz)

We have continued our studies of shock-induced effects in meteorites, their shock histories and the correlation of these histories with other physical and chemical properties. Our study (in conjunction with Professor R. B. Gordon of the Geology and Geophysics Department at Yale) of shock-hardening of α-iron and its possible utility as a shock-barometer in meteorites has been published (paper b on attached list). We have also reported (paper e on attached list) that stony-iron mesosiderites as a group are generally unshocked despite the fact that they seem to have been derived from depths of 500-600 km in their parent body. These results severely limit the locations of possible parent bodies, arguing for a near-Earth parent but not the moon. We are currently conducting a study of shock effects in numerous samples of the Odessa meteorite designed to examine impact dynamics of the crater-forming event.

**Support:** NASA grant 15-005-140

**Isotopic Composition of Vanadium** (Rey and Lipschutz)

We have concluded our study (in conjunction with Dr. H. Balsiger of the Physikalisches Institut, Bern, Switzerland) of the vanadium isotopic composition (a sensitive monitor for energetic charged-particle irradiation) in lunar material - including samples from Apollo 11, 12, 14 and 15 (papers a and f on attached list). We find small differences in the isotopic composition of vanadium from lunar and meteoritic samples which we attribute to instrumental causes. To confirm this we are presently completing similar studies of additional naturally-irradiated, gas-rich meteorites. Our lunar
Studies of Apollo 12, 14 and 15 samples also included determination of Fe, Cr, Mg, Ti and V designed to study the selenochemistry of V and it appears that the concentrations of Cr and Fe parallel that of V in lunar basalts and fines.

Support: NASA grant 15-005-140

Publications:


Talks:


ENDOR Studies of Semiconductors. (Mieher, Fun)

The objective is to experimentally measure and to compare with theory the hyperfine interactions between the host lattice nuclei and electrons or holes trapped at impurities and radiation damage defects in semiconductors.

We have obtained ENDOR data on $\text{Si}^{29}$ lattice nuclei near interstitial iron in silicon. The data confirms that the iron is indeed in an interstitial position. Associated theoretical work on the hyperfine constants is in progress.

The principal investigator and Dr. J. L. Ivey (now at Aerospace Research Laboratories) have made the first successful theoretical calculation of the anisotropic hyperfine constants of $\text{Si}^{29}$ lattice nuclei near shallow donors in silicon. This was done using a ground state shallow donor wavefunction that was expressed as an expansion in terms of Bloch functions for several energy bands throughout the Brillouin zone. Also, it was necessary to use an LCAO representation of the Bloch function since pseudopotential Bloch functions orthogonalized to $\text{Si}^{4+}$ ion cones did not have sufficient 3d character to explain the anisotropic hyperfine interactions.

Support: National Science Foundation GP - 15799 - Al; National Science Foundation and Purdue Materials Research Laboratory

ENDOR Studies of Defects in Ionic Crystals (Mieher, Chung)

The objective is to determine the geometry of radiation damage defects in ionic crystals, to study associations between radiation defects and impurities, and to investigate both experimentally and theoretically...
the hyperfine interactions between host lattice nuclei and trapped electrons and holes.

The technique of electron-nuclear double-resonance (ENDOR) is used to study the defects produced by X-ray or electron bombardment. ENDOR studies of Fe⁺ with and without a charge compensating vacancies have been made and analyzed.

Support: National Science Foundation GP - 15799 - Al

ESR Studies of Metal Oxides (Mieher, Bhartia)

Several ESR resonances have been observed in single crystals of Ti₂O₃. These investigations are continuing in an effort assign models to the paramagnetic centers and to correlate the resonances with other theoretical and experimental work on Ti₂O₃.

Support: National Science Foundation and Purdue Materials Research Laboratory

Publications:


Talks:


Ph.D. Theses:

Mechanism of Production of Metastable States in Electrical Discharge, Molecular Dynamics of Laser Pumping and Gas Dynamic Visible Lasers (E. Leasure)

Research has continued on the use of molecular beam source for metastable atoms and molecules.

The source consists of a conventional supersonic beam source constructed from a machinable ceramic material. When a high D. C. positive voltage is placed on a needle near the nozzle aperture, a glow discharge is initiated both between the needle and the nozzle and outside of the aperture. An extremely efficient conversion of pump power into production of metastable atoms occurs (10 - 50%). A large fraction of the atoms (possibly up to 10% at high pump powers) are excited to the metastable state.

At low pressures, these atoms are translationally hot, (0.5 e.v. kinetic energy). At higher pressures supersonic beams (velocity selected) are produced. Scientific applications of these beams are in elucidation of the molecular dynamics of laser pumping. There may also be direct practical applications in the use of these sources in gas dynamic visible and u.v. lasers.

Support: PRF

Publications:

Talks:
Noise Emission and the Electrical Properties of Amorphous Si and Bi-Si Thin Films (Neudeck, Stricker, & Liedl)

The primary purpose of this research was the investigation of the electrical transport mechanisms and the density of states of amorphous-silicon (a-Si) semiconducting thin films. Additionally, silicon-bismuth (Si-Bi) thin films were studied in order to determine how the addition of small atomic percentages of Bi effects the transport mechanisms and density of states function. The primary electrical measurements include the current noise spectral density, temperature dependence of the d.c. resistivity, and the frequency dependence of the a.c. conductivity. The use of the current noise spectral density, specifically due to generation-recombination noise, provides a new, unique method of gaining information on the conduction mechanisms in amorphous semiconductors.

The samples were prepared by vacuum evaporation from two independently rate-controlled sources in an oil-diffusion pumped system. The substrate material was Corning 7059 glass with pre-deposited Al contact electrodes. The films were deposited on water-cooled substrates and annealed in situ at 400°C for 4 hours immediately after deposition.
All samples were nominally 8000 Å thick. A-Si films were deposited at rates ranging from 3.30 to 6.10 Å/sec. Si-Bi alloy films were deposited at constant Si deposition rate and composition from sample-to-sample was controlled by adjusting the Bi deposition rate. Compositions ranged from zero to 8.13 at % Bi. The two-terminal sample resistance was measured in situ in the temperature range of 400 to 240°C, and all subsequent measurements were made after removal of the samples from the deposition system.

The results indicate that conduction in a-Si is dominated by the transport of electrons. At elevated temperatures, electron transport in extended states above $E_c$ dominate the conduction process. The slope of log $\rho$ vs. $1/T$ is associated with $(E_c - E_F)_0$ and is a strong function of deposition rate. The density of states at $E_c$ was found to be $4 \times 10^{20}$ cm$^{-3}$ eV$^{-1}$ independent of deposition rate, and the position of $E_F$ is determined by the density of localized states associated with structural defects. The slope of log $\rho$ vs. $1/T$ at room temperature and below was .14 eV independent of deposition rate, and conduction in this range is associated with electron hopping via localized states at $E_F$ where .14 eV represents a hopping energy on the order of half of the width of the defect band at $E_F$.

At room temperature, conduction in a-Si is dominated by electron hopping in the localized states of the defect band at $E_F$. However, electron transport in the extended states also contributes to the conduction process as demonstrated by the existence of generation-recombination (g-r) noise, and the temperature and frequency dependence of the a.c. conductivity.
The most significant result obtained was the observation of g-r noise due to a single discrete trapping level found to be approximately 0.17 eV below $E_c$.

The addition of small atomic percentages of Bi caused a smooth decrease in resistivity as a function of composition. The results indicate that conduction is dominated by the transport of electrons; however, the mechanisms involved remain unclear. The observed current noise spectral density is 1/f in nature and possibly attributed to a continuous distribution of localized states in the gap associated with structural disorder caused by Bi.

Support: NSF-MRL GH33574A1

Field Effect Conductance Modulation of Amorphous Silicon Films
(Neudeck, Malhotra)

The objective of this research is to study and determine the effective density of states function in the bandgap of amorphous materials, namely silicon. The approach to the problem has been from a theoretical and experimental viewpoint. The field effect conductance measurement enables the Fermi level to be swept through part of the bandgap near the surface of the thin film. Using fabrication parameters attainable by standard processing the computer calculations predicted a change in conductance should be observable if the surface were less than $10^{13}/\text{cm}^3$ (uniform) and that the density of trap states (also assumed uniform) were less than $10^{19}/\text{cm}^3$. The calculations also indicated the mobile carriers should not significantly effect the result.
Initial experiments were performed with amorphous silicon deposited on glass substrates at 5 Å/sec and annealed for 4 hr. at 400ºC. Aluminum source drain contacts were then evaporated on the amorphous Si. A gate electrode of Al was placed opposite the film on the other side of the glass. A change in conductance of 3 to 1 was measured and was very time dependent. To be able to obtain more conductance modulation and to stop ionic motion the fabrication procedure was changed. We now fabricate the structure by phosphorous doping small gate areas in a single crystal P type silicon wafer (1.5" diameter) this is followed by a growth of 2000 Å of ultra clean oxide that is phosphorus "gettered" to stop ionic motion. The amorphous silicon film is then evaporated and annealed in the clean vacuum system. After removal from the vacuum system, Al source-drain contacts are placed on the A-silicon.

Swept & d-c type field effect has been observed. The more reliable measurement is d-c taking the data immediately after applying the gate voltage change and several minutes later. Four orders of magnitude in sample current have been observed by this method. The data analyzed to date allows about .4 ev of the bandgap to be swept and that the conduction is definitely by electrons.

The effect of annealing and the deposition rate on the shape of the defect states in the bandgap is very pronounced. The lower the deposition rate and/or the longer the anneal time, the lower the density of defect states.

Our present efforts are now being directed towards the effect of temperature on the conductance modulation and to determine the energy
difference between the extended states and the Fermi level. The con-
ductance of the sample vs. 1/T, conductance vs. frequency, and generation
recombination noise will be used to augment the field effect measurements.
The final experiments will be conducted on films with small amounts of
Bismuth added to see what effect compositional disorder has upon the
density of defect states.

Support: NSF-MRL CH33574A1

High Current Density and Failure Models for Semiconductor Devices
(Neudeck, Thompson, Kriegel, and Razouk)

The primary objective of this research is to be able to predict
junction failure due to a very intense current pulse applied across
the terminals of a solid state device. The intensity of the pulse
and the pulse duration necessary for failure is to be modeled from
fundamental device and material parameters.

After a study of the more relevant journals, it was determined
that the failure in junction devices would occur when the junction
was reverse biased (avalanche burnout and/or second breakdown), for-
ward biased (Thermal burn-out and/or second breakdown), or under
conditions of mechanical failure (fusing of the metallization,
migration open or short, and oxide breakdown).

Other than mechanical failure, both the response and the failure
problems are basically associated with the junction thermal properties.
There are two junction temperatures (and current densities to yield
those temperatures), of concern. One temperature will cause permanent
degradation of the v-i characteristic and the other leads to complete failure (open or short). Both effects cause the circuit to malfunction, or at least not operate to specification. The failure mechanisms, once established, yield the current levels for failure; and then the problem of modeling the device at these levels can be approached.

A very simple model for the thermal properties of the device consists of resistance and capacitance analogs of the thermal circuit. The thermal resistance and capacitance of the thermal model can be measured with relative ease for existing devices. First the junction temperatures and leakage current are calibrated by heating the device in an oven and measuring $I_{CO}$ as a function of temperature. Then, with the device in an operating mode, the junction is allowed to heat to a stable condition. The diode is then quickly switched off in a way such that $I_{CO}$ vs. time can be measured. This yields a plot of $T_j$ vs. time. A plot of this data on semi-log paper yields the largest $\tau_1$ (the straight line), $\theta(\Delta T/P)$, and $\phi$ (from $\tau$ and $\theta$). Any temperature deviations from the first straight line (usually for small time increments near zero) are re-plotted. This yields $\tau_2$, when the time scale is greatly expanded. The number of $\theta$-$\phi$ sections can continue until no more data is able to fit a straight line on semilog paper as the time scale is expanded.

Second breakdown is a transition to a state of higher conductance and lower voltage and can occur in both forward and reverse biased junctions. It occurs at high current densities and may be accompanied by device degradation. It is primarily a thermal phenomenon but may be enhanced electronically. When the junction is in the second breakdown region it will cause permanent damage only when the pulse duration
is long enough to create the melt channel. The melt channel causes the v-i characteristic to appear like a large resistance in parallel with the junction.

There appear to be two temperatures of concern to this problem: the junction temperature at which the device will make the v-i transition into second breakdown, and the temperature at which the melt channel is formed. The former is to be used for v-i characteristic modeling while the latter will be used to predict permanent damage. Therefore, the fundamental problem is to predict or determine the temperature at which the junction will go into second breakdown and then to determine the effective junction temperature at which the melt channels form.

Our present efforts are to measure the thermal properties and to computer simulate the junction temperature for various pulse intensities and pulse widths.

Support: Rome Air Development Center & Air Force Weapons Laboratory F306-62-72-C-0438

Publications:

PH.D. Thesis:

"An Experimental Investigation of the Transport Mechanisms & Density of States of Amorphous Silicon and Silicon-Bismuth Thin Films."

R. E. Stricker.
Superconducting Sampler (Newhouse and Bond)

Superconducting amplifiers are the most sensitive detectors of energy, but their frequency response is limited by the uncertainty principle which sets a lower limit to the time in which a given amount of energy can be detected. It has been possible to bypass this limitation for repetitive waveforms by adapting a form of the sampling principle which is well known at room temperature. In this principle a waveform which is of too high a frequency to be amplified by the amplifier under consideration is sampled periodically by a very high speed switch. The sample values are stored in a capacitor for a period which is long enough for the lower frequency amplifier to be able to amplify them. In this manner a repetitive wave form can be displayed by an amplifier whose frequency response is far too low to amplify that wave form in a normal manner. The limitation mentioned earlier is also not contradicted, because the measurement is carried out over many short intervals whereas the uncertainty principle only applies to a single short interval.

Since it is easy to set up persistent currents in superconducting circuits, we use a persistent current circuit instead of a capacitor as a storage element for our sampled signal. With a circuit of this type
we have now been able to demonstrate that the effective bandwidth of an ultrasensitive superconducting cryotron amplifier can be increased by many orders of magnitude by use of a persistent current sampling loop. This principle should be applicable to any superconducting amplifier and should therefore greatly increase the upper frequency range of these ultrasensitive low temperature amplifiers.

Support: NSF-MRL Grant No. GH-33574

Development of An Anisotropy Surface Wave Beam Steering Device Using Semiconductor Enhancement (Newhouse, Davis, Lee and Gunshor)

The anisotropy beam steering concept, first studied theoretically by Newhouse, C. L. Chen and Davis, has here been applied for the first time to a novel device. This acoustic surface wave device is a type of directional coupler which has the novel feature that it can be turned on or off. The utility of beam steering phenomena which depend on non-linear interactions would be considerably limited because of low amplitude outputs, were it not for the technique for increasing the strength of non-linear interactions by the use of a semiconductor which was pioneered by Gunshor and Lee. The demonstration of beam steering in a device application potentially opens up a whole range of applications for this effect, particularly when used with semiconductor enhancement.

Support: NSF-MRL Grant No. GK-11958
Dispersive Beam Steering  (Newhouse and Furgason)

This beam steering technique which is the dual of the anisotropy type has now been demonstrated for dispersive media. We have shown that it is possible to use acoustic plate waves in very thin plates for this purpose. This system offers a very rich and complex frequency-wave number diagram which makes many types of multi-phonon interactions possible. Much work has been done in the last few years outside Purdue University on using the nonlinear interactions of acoustic waves for signal processing. Our demonstration that these functions as well as beam steering can be performed in thin plates which offer a remarkably large range of parameters and conditions because of the complexity of the frequency wave number diagram, may find considerable application in devices because of the increased design alternatives offered to the device engineer. These phenomena should be particularly valuable using the semiconductor enhancement technique also pioneered at Purdue.

Support: NSF-MRL Grant No. GK-36533

Random Signal Ultrasonic Flaw Detection (Newhouse and Bendick)

Ultrasonic flaw detection, although widely used in industry, has been limited in the range of the test objects that it can cope with. For instance, it has a very limited use on concrete structures because of high sound absorption and cannot be used adequately on the very thick metal structures used in the largest electrical generators. Our techniques of using a random signal which are adapted from some originally developed
for radar, promised to overcome many of these limitations and, combined
with a new geometrical technique for avoiding clutter reflections, may
also lead to an order of magnitude improvement in the smallness of the
imperfections that can be detected with ultrasound. Thus the technique
may lead to industrial improvements in flaw detection and may also have
scientific impact if it proves possible to detect inhomogeneities on the
grain boundary scale.

Support: ARPA Grant No. DAHZ 15-73-G12

Publications:
"Convolution and Correlation Using Nonlinear Interactions of Lamb Waves,"
E. W. Furgason and V. L. Newhouse, IEEE Trans., Son. Ultrasonics, SU-20,

"Steering Acoustic Surface Waves by Nonlinear Mixing," K. L. Davis and

"Some Superconductive Thin Film Devices for Radio and Microwave Frequencies,"
p. 673.


"Interactions between Slow Circuit Waves and Drifting Carriers in InSb
and Ge at 4.2° K," J. C. Freeman, R. L. Gunshor and V. L. Newhouse, Appl.
Talks:


Reports:

Ph.D. Thesis:
Photophenomena in MIS Structures (Pierret & Roesner)

Objective: Observe and characterize photo-excitation from surface centers in the MIS system.

Approach: Measure and analyze the time dependent capacitance at constant voltage of an MIS-capacitor which is maintained at 77°K and subjected to monochromatic infrared radiation.

Progress: We have successfully developed a technique whereby photoemission from surface centers can be effectively isolated and carefully monitored. We have made what is believed to be the first observation of photoemission from surface centers in the extensively studied Si-SiO$_2$ system and the first experimental determination of photocapture cross sections ($\sigma_N^*$) for surface centers in any system. For the Si-SiO$_2$ system $\sigma_N^* < 10^{-18}$ cm$^2$, is essentially independent of bandgap energy and decreases exponentially with the surface center SiO$_2$ positioning relative to the Si-SiO$_2$ interface. Furthermore, of prime significance in the electrical modeling of surface centers, our data supports the viewpoint that surface centers are distributed into the oxide from the Si-SiO$_2$ interface and rejects the viewpoint that a $S$-function of states exists right at the Si-SiO$_2$ interface.

Support: NSF Grant GH-33574 and GH-33574A1
Separation and Characterization of Carrier Generation Mechanisms Using the MIS-C (Pierret & Small)

Objectives: Separate and properly characterize carrier generation occurring in deeply depleted Metal-Insulator-Semiconductor structures.

Approach: A detailed analysis is made of electrical characteristics derived from MIS-C test vehicles subjected to a combination of deep depletion probing techniques (linear-sweep, C-t transient and lateral flow).

Progress: There are three basic mechanisms which can operate to create carriers in deeply depleted MIS structures; namely, lateral surface generation, gated surface generation and depletion region generation. We have exhibited and reported the effect of lateral surface generation on observed characteristics and have successfully minimized this generation component using guard-ring structures. We have exhibited both experimentally and theoretically that gated surface generation is typically negligible and, when important, is improperly characterized in the scientific literature. Although the analysis is incomplete at this time, our data also suggests that the minority carrier lifetime used to characterize depletion region generation is dependent on the width of the depletion region and is the major reason for large variations in the observed generation rates deduced from similarly fabricated structures.

Support: NSF grant GH-33574 and GH-33574A1
Publications:


The purpose of this research is to develop a rapid and non-destructive method for the analysis of impurities in metal foils and for the determination of their location in the host material. The approach involves the measurement of protons and α-particles emitted in nuclear reactions induced by light ions. The technique is especially useful for the detection of light elements, such as hydrogen, carbon, and oxygen, because of the unique energies of the particles emitted in nuclear reactions of these elements.

The present sensitivity of the technique is about 2ppm oxygen and 5ppm hydrogen and carbon. It is also possible to distinguish between adsorbed impurities and those diffused throughout the body of the foil by observation of the shape of α-particle lines at high resolution. The use of heavy ion projectiles, such as $^{16}O$, appears to be particularly promising in localizing impurities.

Support: NSF - 7662, AEC - 7247
Normal Vibrations in RNA and DNA (Eyster, Prohofsky)

The vibrational spectrum of polyuracil has been calculated in the A conformation. Work is proceeding on other compounds. A method to simplify the calculations by breaking up large molecules into smaller parts and then finding the normal modes of the original molecule by a Green's function calculation has been developed. The usefulness of method is being investigated.

Support: PRF-XR 7431

Giant Oscillations in Ultrasonic Attenuation (Rohlfing, Prohofsky)

The thrust of this project has shifted and the title is no longer appropriate. A more appropriate title might be "The Hot Electron Problem in Quantizing Magnetic Fields." The reason for this shift is that our initial calculation show the oscillation in acoustic gain that occurs when the landau level separations become comparable to optical phonon energies are caused by a cooling of the hot electrons by the optical phonon heat capacity. We are currently attempting to calculate the hot electron distribution in greater detail. We have set up a set of coupled equations for the calculation of both the temperature and drift velocity separately for each landau level. Such detailed knowledge of the electron distribution will allow us to calculate the phonon emission more accurately and investigate the possibility of stimulated optical phonon emission. We find that the temperature of all the landau levels increases and fluctuates with changes in magnetic field. We also find surprisingly that some higher landau levels have counter currents flowing in them although the magnitudes of these currents are small and do not alter the total current. This implies that optical phonons of $q > 0$ are the dominant relaxation mechanism in some cases.

Support: NSF-MRL GH 33574
Laser Raman and Brillouin Scattering in Solids: Piezospectroscopic Study of the Raman Spectrum of α-Quartz (Ramdas, Rodriguez and Tekippe)

The effect of uniaxial stress on the Raman spectrum of α-quartz is investigated at liquid helium temperatures using a quantitative stress cryostat. Stresses up to ~ 10 kbar were employed. The E(LO+TO) doubly degenerate Raman lines with no LO-TO splitting, viz., the 128 cm\(^{-1}\), 263 cm\(^{-1}\), 695 cm\(^{-1}\) lines split into two components when the applied compressive force, \(F\), is along a direction other than the trigonal axis. The polarization features of the stress induced components can be explained on the basis of the reduced symmetry of the crystal under uniaxial stress. The positions of the stress induced components of the 128 cm\(^{-1}\) line are linear with stress. Degenerate perturbation theory utilizing a deformation potential linear in strain permits the stress effects for the E(LO+TO) lines in different crystallographic directions of \(F\) to be correlated in terms of four deformation potential constants; these have been determined for the 128 cm\(^{-1}\) line to be \(a = -218\), \(b = -58\), \(c = \mp 174\) and \(d = \pm 160\) in units of cm\(^{-1}\) per unit strain. The LO components of the LO-TO doublets at 393-400 cm\(^{-1}\), 796-805 cm\(^{-1}\) and 1064-1232 cm\(^{-1}\) show a shift to higher frequencies whereas the TO components remain at their zero stress positions. The deformation potential theory predicts a linear shift with stress for lines of \(A_1\) symmetry, the shift being characterized by two deformation potential constants. These constants have been determined to be \(e = -814\) and \(f = -1000\) in units of cm\(^{-1}\) per unit strain for the 205 cm\(^{-1}\) line of \(A_1\) symmetry. The shift of the other lines of \(A_1\) symmetry, viz., the 354 cm\(^{-1}\), 464 cm\(^{-1}\), and 1081 cm\(^{-1}\), lines, is less pronounced than that of the 205 cm\(^{-1}\) line.
**Effect of Uniaxial Stress on the Raman Spectra of Cubic Crystals: CaF$_2$, BaF$_2$, and Bi$_{12}$GeO$_{20}$.**

(Ramdas and Venugopalan)

The effect of uniaxial stress on the first-order Raman spectra of the cubic crystals, CaF$_2$, BaF$_2$ and Bi$_{12}$GeO$_{20}$ is studied at ~150 K using a quantitative stress cryostat. Both CaF$_2$ and BaF$_2$ belong to the space group O$_h^5$ (Fm3m) and possess a single, triply degenerate, Raman-active zone-center optical phonon of F$_{2g}$ symmetry. In contrast, Bi$_{12}$GeO$_{20}$ has a very rich first-order Raman spectrum consisting of lines of A, E, F and LO-TO split F modes. The effect of uniaxial stress on the F$_{2g}$ line of CaF$_2$ and on Raman lines typical of the different symmetries in Bi$_{12}$GeO$_{20}$ is studied up to 7 kbar with compressive force, \( \vec{F} \), along [001], [111] or [110].

The Raman line of BaF$_2$ is studied up to 2.4 kbar for \( \vec{F} \parallel [001] \). The stress-induced splittings and polarization characteristics in each case can be understood on the basis of the reduced symmetry of the crystal under applied stress. Using a perturbing Hamiltonian linear in strain, the secular equation is derived for phonons of each symmetry in terms of phenomenological "deformation potential constants". Phonons of A, E, F symmetry in T and of F$_{2g}$ symmetry in O$_h$ are characterized by one, three, four and three deformation constants respectively. Within the framework of this theory, the splittings as a function of the crystallographic orientation of the applied force can be correlated in terms of the deformation potential constants, whereas the intensities of the stress-induced components can be calculated in terms of the zero-stress polarizability tensor components. Experimentally, in all the cases the positions of the stress-induced components are observed to vary linearly with stress and the splittings, shifts and polarization characteristics are consistent with the predictions based on the reduced symmetry of the crystal as well as the deformation potential approach. On the basis of the observed polarization characteristics of the stress-induced components, appropriate eigenvalues have been associated with them and the deformation potential constants have been obtained for all the lines studied.
Support: National Science Foundation (GH32001)  
National Science Foundation-Material Research Laboratory (GH33574)

Publications:


Also see under Fisher, Ramdas, and Rodriguez; Fisher and Rodriguez; Rodriguez.

Talks:


Also see under Fisher, Ramdas and Rodriguez; Fisher and Rodriguez; Rodriguez.

Ph.D. Thesis:

Bonding and Spectra in Transition-Metal Clusters (Richardson and Blackman)

Work continues in extending the theoretical study of electron delocalization and spectra to compounds of the second transition series elements. Emphasis is being shifted more to predictions, since, as compared to analogous compounds of the first series, much less experimental data have been accumulated so far. With the systematic set of analytic atomic orbitals (AO's) now available for atoms and ions of the second transition series, as indicated in the last Technical Report, various works have begun in this general area.

At the outset we commenced to survey and compare the various properties of the 3d and 4d series AO's that are of significance in determining the extent of their interaction with various ligands. In addition to the experimentally-known ionization potentials and spin-orbit coupling constants, we are examining the important d-d electrostatic interaction integrals, electron correlation effects and orbital overlaps and interactions with typical ligands. Already, a number of uniform differences between +2 and +3 ions of the two series have been calculated. This work continues with the arrival of Dr. L. Pueyo, who will also relate the observations to be made to general chemical data already known.
With the theoretical details of atomic wave functions now available, an investigation of the satellite structure in the 3d region of the ESCA spectrum of Ag complexes was begun. A computer program has been written to predict energies of all states arising from the relevant $\text{Ag}^{+2} \ 3d^94d^9$ configuration. $3d-4d$ electrostatic interaction integrals are taken from our atomic SCF orbital calculations; an adjustable spin-orbit interaction is included; and an arbitrary crystal field perturbation is provided. Diagonalization of the complete 100x100 matrix is then effected. To each of the states thus calculated is applied an approximate transition probability factor. All line broadening effects are ignored, except that finally the complete manifold of computed states is convoluted with a triangular slit function of adjustable width. This study will proceed by comparing the predictions of various assortments of adjustable parameters to the ESCA satellite spectra obtained by Professor Walton of this Department.

Here, and in many other laboratories now, a considerable amount of effort has been directed toward obtaining reasonably accurate LCAO MO SCF wave functions and energies for simpler complex ions of the first transition series. The generally good success there prompts us to discover whether similar methods yield equally valuable results for the later series. This effort is important also in connection with extending tight-binding band structure calculations to compounds of these elements.

Partly in connection with other theoretical investigations of diatomic molecules, our earlier computer program which evaluates required two-electron electrostatic repulsion integrals has been replaced with a
newer version. Some of the other necessary programs have also been rewritten; the entire sequence of calculation has been checked by recalculations on some of the first series of compounds studied earlier. Because we must evaluate the significance of the three-times larger spin-orbit interaction, this effect is now being included in the final calculation of excited state energies.

Underway at present are calculations on the MoF$_6^-$ systems which are designed to investigate the quality of the results with reference to experiment and with detailed comparisons with the analogous CrF$_6^-$ system.

Support: NSF/MRL

Electronic Band Structure Calculations for Ionic Solids (Richardson and Lieb)

Following our earlier consideration of SrTiO$_3$, using an SCF tight binding approach to its electronic band structure, attention has been directed to some binary oxides having the corundum structure. Interpretation of the metal-insulator transition and various other physical properties of Ti$_2$O$_3$ and V$_2$O$_3$, for instance, has led to some conjectures about what might be their band structure. Nebensahl and Weger have calculated a band structure for these materials including metal-metal interactions in a tight-binding approximation but excluding the nearest-neighbor interactions between metal and oxygen ions. In view of our experience with SrTiO$_3$ and the culmination of experience with isolated
transition metal complex ions, this is a very serious approximation in eliminating the primary perturbations upon the electronic states of the metal ions.

We are setting up the tight-binding calculation including nearest-neighbor metal-oxygen and metal-metal interactions. These various interactions (overlap and transfer integrals) at the outset are to be treated as adjustable parameters. Key features in the band structure, in particular the presence of any gaps in the 3d bands, will be investigated as a function of those parameters and also the internuclear distances within the corundum structure.

Analysis of the computational procedures has been completed. Assembling the computer programs to treat this problem with an atomic orbital basis comparable to that used for SrTiO$_3$ is now in progress.

Support: NSF/MRL

Publications:

Studies Leading to the Synthesis of High Temperature Resistant Polymers (Robinson, Swanson)

A modified series of potential catalysts containing Mo or W, an NO group, a Cl, two CO groups and two additional ligands has been prepared and characterized. The reaction of M(CO)$_3$(CH$_3$CN)$_3$ (M = Mo or W) in tetrahydrofuran under nitrogen with sufficient nitrosyl chloride to just dissolve the solid metal carbonyl produces a dark brown solution, from which may be isolated either M(CO)$_2$(NO)$_2$Cl or M(CO)(NO)(CH$_3$CN)$_2$Cl by addition of the appropriate ligand. The intermediate in the synthesis appears to be M(CO)$_2$(NO)(CH$_3$CN)$_2$Cl. In the majority of the compounds examined, the ligands are bound too tightly for the metal to function as a catalyst. However, in those compounds with acetonitrile ligands, the nitrogen-metal bonds are sufficiently weak that those ligands are readily displaced by substrate with resulting polymerization of the substrate. The condensation of acetylenes to oligomeric products has been observed, but no high polymers were produced.

Support: NSF-MRL and NSF-GP 17554

Single Crystal X-ray Diffraction Studies (Robinson, Honig, Vest and Smith)

The Crystal Structure of Ti$_2$O$_3$ and (Ti$_{1.000V_{0.100}203$. The crystal structures of the semiconductor Ti$_2$O$_3$ and the semimetal (Ti$_{0.900V_{0.100}203$ were determined from x-ray diffraction data collected from single crystals.
The compounds are isostructural with Al$_2$O$_3$ with rhombohedral unit cell dimensions of $a = 5.4325(8)$ Å and $a = 56.75(1)^\circ$ for Ti$_2$O$_3$ and $a = 5.4692(8)$ Å and $a = 55.63(1)^\circ$ for the doped system. The effect of substitution of V$^{3+}$ is to increase the metal-metal distance across the shared octahedral face from 2.579 Å in Ti$_2$O$_3$ to 2.658 Å in (Ti$_{0.900}$V$_{0.100}$)$_2$O$_3$ while decreasing the metal-metal distance across the shared octahedral edge from 2.997 Å to 2.968 Å. The metal-oxygen distances exhibit only small changes. These structural changes are consistent with the band theory proposed by VanZandt, Honig, and Goodenough (1968) to explain changes in electrical and other properties with increasing vanadium content in (Ti$_{1-x}$V$_x$)$_2$O$_3$.

The Crystal Structure of Gd$_{0.992}$TiO$_3$.— The structure of Gd$_{0.992}$TiO$_3$ has been determined by single crystal x-ray diffraction techniques. The structure has been found to be identical to that reported for GdFeO$_3$ but with random Gd vacancies. The only significant differences are found between the Fe-O and Ti-O distances. The Fe-O distances in the distorted FeO$_6$ octahedron are 2.000(4), 2.030(4), and 2.010(4) Å while the corresponding Ti-O distances are 2.007(4), 2.027(4), and 2.057(4) Å.

Support: NSF-MRL and NSF GP 28052

Publications:


Group-Theoretical Study of Double Acceptors in Semiconductors Under Uniaxial Stress  
(E. Kartheuser and S. Rodriguez)

We have made a study of the energy splittings, selection rules, and relative intensities of the optical transitions associated with neutral group-II acceptors in group-IV semiconductors under uniaxial stress. The exact discussion is simplified by describing the double acceptor in a self-consistent-field approximation. Our treatment is applied to the analysis of experimental results for neutral zinc in germanium under uniaxial stress parallel to the directions (100) and (111). A comparison with the experimental work of Jones and Fisher permits us to determine the level ordering under stress. The relative intensities of the stress-induced D lines can be fitted, in this approximation, with only two real parameters.

Support: National Science Foundation - Materials Research Laboratory GH 33574, National Science Foundation GH 32001, and National Science Foundation GH 33774.


The dynamical dielectric response of a condensed system of molecules with permanent electric dipole moments is studied. We start from the dynamical extension of the Onsager theory developed by Nee and Zwanzig, but generalized so as to be applicable at high frequencies. Specifically, we retain inertial terms and introduce relaxation effects in a way valid in a high frequency limit. The dielectric function obtained incorporates a diversity of both collective and single-particle behavior, consistently, over the entire range of frequencies below those of intramolecular excitation.
It is noteworthy that not only is a collective mode, or, dipolar plasmon, exhibited, but that its frequency is also a resonance of the single-dipole motion. The properties of the dielectric function are analyzed and illustrated in detail, and specific applications are made to water, to hydrogen chloride, and to chloroform.

Support: National Science Foundation, GK 33774; National Science Foundation GH 32001

Publications:


Talks:


See also under: A. K. Ramdas and S. Rodriguez;
         P. Fisher, A. K. Ramdas, and S. Rodriguez;
         P. Fisher and S. Rodriguez
Electrical Properties of the Semiconductor Insulator Interface (Schwartz and Cooper)

A distributed parameter numerical model has been developed which describes the small signal conductance, capacitance, and noise due to a continuum of surface states at the Si-SiO₂ interface. The model includes both majority and minority carrier transitions and is valid in all bias regions: depletion, midgap and weak inversion. The predictions of the model have been compared to measured surface state conductance and good agreement has been obtained in all bias regions.

This model has been used to predict the noise voltage which would be generated by an MOS capacitor. The results agree very closely with experimentally measured noise.

Electron captured cross sections have been measured and were observed to vary from sample to sample in range from $1 \times 10^{-15}$ cm$^2$ to $3 \times 10^{-14}$ cm$^2$. Capture cross sections were found to be independent of the energy in the midgap region and well into weak inversion. Hole capture cross sections, in weak inversion, as small as $2 \times 10^{-17}$ cm$^2$ were observed. The ratio of the electron to hole capture cross sections is found to be dependent, to first order, on the surface state density, and independent of the crystal orientation, substrate doping level, and annealing procedures. This ratio was found to depend as the inverse
three halfs power of the surface state density in the range from \(1 \times 10^{10}\) ev\(^{-1}\) cm\(^{-2}\) to \(5 \times 10^{11}\) ev\(^{-1}\) cm\(^{-2}\).

**Support:** National Science Foundation Grant GR33574, Atomic Energy Commission.

**Germanium Thermophotovoltaic Cells** (Schwartz, Gardner & Lammert)

Planar p-i-n germanium photovoltaic cells have been fabricated according to the design criteria developed during previous computer studies of thermophotovoltaic systems. Computer studies indicated that cell conversion efficiencies as high as 50\% with monochromatic illumination and as high as 14\%\% from an \(\text{Er}_2\text{O}_3\) radiation source operating at 1,800\,C, could be obtained.

Such cells have now been fabricated. These cells are considerably less efficient than the theoretical studies would indicate. The reduction in efficiency appears to be due to surface recombination on the illuminated face of the cell. This occurs even though the surface recombination velocity at the illuminated surface is extremely small under low intensity illumination (less than 1 cm sec\(^{-1}\)).

Possible means of reducing the surface recombination velocity have been investigated. These include the use of a transparent field plate on which a bias is applied to force the surface toward accumulation. Experiments indicate that this can result in a factor of three reduction in the surface recombination velocity.

Other techniques which were used include the use of ion implantation to give a highly doped surface. These experiments have been only partially successful.
Work is continuing on the problem of reduction of the surface recombination velocity to levels which are acceptable for device operation.

Support: U. S. Army Materials Contract No. DAAB07-70-C-0129

Talks:
"Surface State Characteristics of the SiO₂-Si Interface in Midgap and Weak Inversion as Determined by the MOS Conductance Technique."


Ph.D. Theses:

Ultrasonic Studies of III-V Semiconductors

**Objective:** To investigate the elastic and piezoelectric properties of some III-V semiconductors with particular emphasis on the influence of mobile charge carriers on these properties.

**Approach:** Measure the velocities, and in some cases the attenuation, of ultrasonic waves between liquid helium and room temperatures in III-V semiconductors which exhibit a large amount of carrier freeze-out at low temperatures.

**Progress:** Velocity and attenuation measurements of 30 MHz ultrasonic waves from 4.2K to 300K have been completed on oriented single crystals of sulfur-doped and nominally undoped, n-type GaP. The velocity and attenuation measurements on piezoelectrically active ultrasonic modes ([110] [001] shear and [111] [111] longitudinal) yielded values for the magnitude of the piezoelectric constant, $|e_{14}|$, of GaP for which no accurate value was previously available. Velocity measurements also yielded the first values of the low temperature elastic constants of GaP. The low temperature elastic constant data also yielded a Debye $\Theta$ of 443.6K.

Attenuation versus temperature curves for the four III-V's studied to date (GaSb, GaAs, InSb, GaP) have been fitted using existing theory and an activated resistivity of the form $\rho = \rho_o e^{E/kT}$. The agreement between the parameters $\rho_o$ and $E$ obtained from those fits and those obtained from resistivity vs. temperature measurements was sometimes quite good (GaP, GaAs) and sometimes marginal (GaSb, InSb). Lack of agreement is, we believe, a manifestation of sample inhomogeneity.

The transfer of electronic bonding charge implied by the values of $e_{14}$ for the III-V's we have investigated and for other zinc blende
compounds was found to depend on ionicity in a way similar to that implied by recent theory. The correlation between bond charge transfer and ionicity was found to be much better when a more appropriate effective charge is used than has been used previously. Successful interpretation of piezoelectric constants in terms of recent microscopic theory provides support for such theory and for the dielectric theory of solids.

Support: National Science Foundation - Materials Research Laboratory
Grant GH - 33574

Elastic Constants and the Electrical Transition in Ti₂O₃ and (Ti₁₋ₓVₓ)₂O₃
(Chi and Sladek)

Objective: To study the elastic properties of materials which exhibit nonmetal-to-metal transitions.

Approach: Determine the elastic constants from the velocities of ultrasonic waves in single crystal samples of Ti₂O₃ and (Ti₁₋ₓVₓ)₂O₃ as a function of temperature in a range which includes the electrical transition. Interpret the results in terms of lattice dynamics and the contribution of Ti 3d electrons to the elastic constants.

Progress: Analysis was completed of the anomalies in the elastic constants of Ti₂O₃ which had been discovered previously by us to accompany the gradual electrical transition in this material between about 400K and 500K. It was found that minima in C₁₁, C₁₂, and C₃₃ and a maximum in C₁₃ could be accounted for semiquantitatively in terms of the contribution of Ti 3d electrons to the elastic constants. This contribution was calculated by means of an electronic computer using a deformation potential approach and two 3d subbands which approached each other and finally overlapped as the temperature was raised through the electrical transition. Values for two deformation potentials were deduced. While interactions of electrons with each other or with the lattice did not appear explicitly in our calculation, they seemed to be implicit in the very large shift of the electronic energy bands with temperature.

The temperature dependence of C₄₄ was accounted for as due to lattice anharmonicity. The reduction in the elastic constant anomalies due to
substitution of V ions for some of the Ti ions was interpreted qualitatively in terms of V causing the 3d subbands to approach each other and finally overlap by the time a 10% vanadium concentration was achieved.

Support: National Science Foundation Grant GH - 33383.

Specific Heat of Single Crystal, Undoped and V-doped Ti$_2$O$_3$. (Barros, Chandrashekhar, Chi, Honig* and Sladek)

Objective: To elucidate the lattice and electronic contributions to the electrical transition in Ti$_2$O$_3$.

Approach: Interpret the heat capacity data of Barros, Chandrashekhar and Honig.

Progress: The anomaly previously measured in the heat capacity of Ti$_2$O$_3$ in the vicinity of the electrical transition (380-550K) by Barros, Chandrashekhar, and Honig was accounted for by means of a computer calculation of the specific heat of electrons in two Ti 3d subbands which approach and overlap with increasing temperature in a manner consistent with that employed by Chi and Sladek for their calculation of the contribution of Ti 3d electrons to the elastic constants. The reduction of the heat capacity caused by substitution of V ions for some of the Ti ions was discussed in terms of the relative motion of electronic energy bands like those used for Ti$_2$O$_3$.

Support: National Science Foundation Grant GH - 33383

Ultrasonic Attenuation and the Electrical Transition in Ti$_2$O$_3$. (Chi and Sladek)

Objective: To clarify the roles played by the electrons, the lattice, and their interactions in giving rise to the semiconductor-semimetal transition in Ti$_2$O$_3$.

Approach: Measure and interpret the attenuation of ultrasonic waves at various frequencies from room temperature up to 500K and higher if possible.

+Members of Prof. Honig's group
*Prof. J. M. Honig, Dept. of Chemistry
Progress: Measurements of the attenuation $\alpha$, in single crystal samples of Ti$_2$O$_3$ were made at various frequencies, $f$, between 30 MHz and 300 MHz for temperatures between 298K and 525K. They revealed that for longitudinal waves traveling in the direction of the a-axis of the crystal the intrinsic component of the attenuation was proportional to $f^2$ at room temperature and that the attenuation of various types of waves went through a maximum in a temperature range close to that where the electrical transition occurs. The maxima in $\alpha$ were interpreted as a temperature dependence of the ratio of anharmonic to harmonic lattice forces due to the change in electronic screening of important interionic interactions by Ti 3d electrons as the overlap and relative populations of the $\alpha$ and $\gamma$ subbands change through the electrical transition. Other possible mechanisms were also considered, but they were unable to account for the attenuation maxima satisfactorily.

Support: National Science Foundation Grant GH - 33383 with some support from National Science Foundation - Materials Research Laboratory Grant GH - 33574 especially in the form of crystals from the Purdue Central Crystal Growth Facility.

Elastic Constants of Ti$_2$O$_3$ and (Ti$_{1-x}$V$_x$)$_2$O$_3$ at Low Temperatures (Bennett and Sladek)

Objective: To study the elastic properties of materials which have nonmetal - to - metal transitions.

Approach: Determine the elastic constants of (Ti$_{1-x}$V$_x$)$_2$O$_3$, where $0 \leq x \leq 0.1$ at low temperatures by measuring the velocities of ultrasonic waves. Compute the electronic contribution to the elastic constants by using a model which explains the extra specific heat at low temperature. Compare the results of measurement and computations to test the model and to see how it may need to be modified or supplanted.

Progress: Measurements of the velocities of 30 MHz longitudinal waves traveling parallel to the a- and c- crystallographic axes have been made on single crystal samples of Ti$_2$O$_3$ and (Ti$_{0.96}$V$_{0.04}$)$_2$O$_3$ down to liquid helium temperatures. The samples were provided by the Purdue
Central Crystal Growth Facility. It was found that $C_{11}$ and $C_{33}$ are substantially less for the V-doped sample than for undoped Ti$_2$O$_3$ at low temperatures, with $C_{33}$ being depressed more than $C_{11}$. These results can be interpreted as an electronic effect in which the stress induced shift of a narrow vanadium impurity band relative to the wide $a_{1g}$ Ti 3-d subband within whose energy range the V band lies.

A narrow V impurity band below the $a_{1g}$ Ti 3-d subband is also invoked in order to account for the location of the Fermi level within the $a_{1g}$ subband. The existence of a set of narrow V impurity bands had been postulated by Van Zandt in order to interpret low temperature heat capacity data of Sjostrand and Keesom. Our computer calculations of the electronic contributions to $C_{33}$ and $C_{11}$ using values for the deformation potentials deduced by Chi and Sladek or by Chen and Sladek for undoped Ti$_2$O$_3$ show that the elastic constants for V-doped Ti$_2$O$_3$ should be lower than for undoped Ti$_2$O$_3$ and that $C_{33}$ should be depressed more than $C_{11}$ as is observed. This seems to imply a qualitative confirmation of the $e_g$ parentage for the V impurity band which overlies the $a_{1g}$ host subband. However, the calculated electronic contributions to $C_{33}$ and $C_{11}$ are about independent of temperature, thus leaving unexplained the observation that $C_{33}$ and $C_{11}$ are less temperature dependent in the V-doped sample than in undoped Ti$_2$O$_3$.

Support: National Science Foundation - Materials Research Laboratory Grant GH - 33574, National Science Foundation Grant GH - 33383.

Piezoresistance Studies in Ti$_2$O$_3$ (Chen and Sladek).

Objective: To obtain information on the nature of the electronic energy bands and, if possible, on the processes by which electrons are scattered in Ti$_2$O$_3$ in order to elucidate the semiconductor-semimetal transition in this material.

Approach: To measure the changes of electrical resistivity caused by uniaxial stress and hydrostatic pressure in oriented, single-crystal, samples of Ti$_2$O$_3$ at various temperatures.
Progress: The change of electrical resistivity, $\Delta \rho$, due to uniaxial compression $X$ applied along the c-axis of the crystal was measured at various temperatures between 300K and 77K. It was found that $\Delta \rho/\rho_0$ was positive and proportional to, or nearly proportional to $X$, and that $\Delta \rho/\rho_0X$ depended most linearly on reciprocal temperature. A measurement of the piezoresistance due to uniaxial compression along the a-axis of the crystal has also been made, but only at room temperature so far.

The above results can be interpreted in terms of stress induced shifts of the $a_{lg}$ and $e_{g}$ Ti 3d subbands -- the subbands moving apart due to c-axis compression and moving towards each other due to a-axis compression. Values deduced for the deformation potentials have the same signs as those deduced by Chi and Sladek (CS) from fitting elastic constant anomalies in the vicinity of the electrical transition, but $A_3$ has a significantly larger absolute value than that deduced by CS. The ratio of the square of the deformation potentials deduced from the piezoresistance data is better able to account for the ratio of the depression of $C_{33}$ to the depression in $C_{11}$ in $(Ti_{0.96}V_{0.04})_2O_3$ relative to that in $Ti_2O_3$ found by Bennett and Sladek at liquid He temperatures.

Support: David Ross Grant, National Science Foundation - Materials Research Laboratory Grant GH - 33574.

Ultrasonic Studies of Amorphous Materials (Ng and Sladek)

Objective: To obtain information about structural and relaxational effects in amorphous materials from ultrasonic studies.

Approach: To measure the attenuation and velocity of ultrasonic waves as a function of frequency and temperature in amorphous $As_2S_3$ and in vitreous hydrogen-bonded media.

Progress: Measurements of the attenuation, $\alpha$, of ultrasonic waves with various frequencies (30, 110, and 150 MHz) in amorphous $As_2S_3$ were extended from 50K down to 1.5K. It was found that $\alpha$ depended about linearly on frequency. At the lowest temperatures $\alpha$ increased more rapidly with temperature the higher the frequency. At higher temperatures, $\alpha$ was almost independent of temperature. The attenuation can be accounted for
quantitatively in terms of the transitions of atoms or ions, probably sulfur, between alternative positions representable by the asymmetric, double potential-energy-well model for glasses in which there are double potential wells with a wide variety of sizes.

Thermal phonon-assisted tunneling through the barrier separating potential wells was found to be the important transition mechanism below 50K. Furthermore, it was found that the attenuation could be accounted for quantitatively using recent theory provided that the number of double-well-potentials exhibited a gaussian-like dependence on the size of the barrier parameter of the well. Our attenuation data between 150K and 300K were accounted for as a relaxation effect due to atoms (or ions) jumping over the barrier between the two wells of a pair. Dispersion in the velocity was observed indicating a nonthermal relaxation process.

Measurements of the attenuation of longitudinal ultrasonic waves in the protonic semiconductor $\text{H}_2\text{Cr}_2\text{O}_7 + 7.16 \text{H}_2\text{O}$ were extended up to 45 MHz in the liquid state. The attenuation became too large to measure in an ever wider temperature interval the higher the frequency in a temperature region around 193K. At temperatures above the region where it had been too large to measure, the attenuation was found to be comprised of two terms -- a background term which was independent of both frequency and temperature and a term proportional to $f^2 \exp (E/kT)$ where $E \approx 0.26$ eV. Below the glass temperature of 159K the attenuation was proportional to frequency as in most glasses indicating a relaxation attenuation characterized by a wide distribution of relaxation times. Our results in the liquid state can be interpreted in terms of the relaxation of the change of proton concentration produced by the ultrasonic wave if certain reasonable assumptions are made about the volume change and recombination rate constant for the dissociation and recombination of $\text{H}_2\text{Cr}_2\text{O}_7$. However, protonic hopping might also provide a possible mechanism for the attenuation. In the glassy state protonic motion between potential wells of the various H-bonds could be responsible for the attenuation provided that the well parameters have a wide distribution of values.
Support: National Science Foundation Grant GH - 33383 and National Science Foundation - Materials Research Laboratory Grant GH - 33574

Publications:


Talks:


Ph.D. Theses:
"Elastic Constants and The Electrical Transition in Ti$_2$O$_3$ and V-doped Ti$_2$O$_3"$, T. C. Chi, December 1972.

Development of an Entropy Production Criterion with Special Attention to Nucleation and Growth (Chasteen and Spitzer)

Systems undergoing spontaneous changes of state follow reproducible paths which are totally determined by the initial conditions, the final conditions, and the system constraints. This fact suggests that all such systems are obeying some general path-defining principle. Principles which define paths involve the extremalization of the integral of some function. The possible principle under current investigation is "the integral of the time-rate-of-change of entropy of an isolated system between any two arbitrary times is a maximum."

Other investigators have attempted to describe the states assumed by non-equilibrium systems. Prigogine proposed that systems tending to steady state assume their minimum value of entropy production at steady state. Cahn and Mullins applied the calculus of variations to heat conduction to deduce the specific temperature profile corresponding to the lowest possible value of entropy production. Because this was not the steady-state profile, temperature configurations exist whose entropy production values are less than the steady-state value.

The conditions under which real systems could assume such configurations remained to be determined. Computer programs for heat conduction written during the current investigation have shown that only those systems which absorb energy during their traverse to steady state display entropy production values prior to steady state less than the steady-state value. Although the values of minimum entropy production for these systems approach the absolute minimum value predicted by the calculus of variations, the temperature configurations do not, in general, approach the specific temperature profile corresponding to the absolute minimum.

Current work is directed toward development of a general proof that only those systems which absorb energy during a traverse to steady state violate Prigogine's Principle and an explanation of the fact that these systems approach, but do not attain, the absolute minimum entropy production value. Such work
should lead to a test of the applicability of the proposed general principle. Such a path-defining principle would be valuable in the description of many rate processes and will be applied specifically to nucleation and growth.

Support: NSF-MRL GH33574

Interpretation of Interface Morphologies Observed During Controlled Solidification (Chen and Spitzer)

Morphologies observed during solidification of metallic alloys are the result of experimental conditions which affect solute concentrations and temperature gradients within the liquid phase. A quantitative description of the interface morphology in terms of controlling variables is of interest as an aid to understanding and controlling the final microsegregation and microstructure of the solid.

An ultrasonic-pulse technique has been successfully developed to reveal interface contours. Very short pulses of ultrasonic energy are directed at the advancing interface at known time intervals. Subsequent metallographic examination reveals narrow contour lines which record the exact shape of the solidification front. This method offers significant advantages over decantation techniques which attempt to interrupt the progress of solidification. Successive profiles and, therefore, the non-steady-state development or decay of a morphology can be observed in a single sample.

The major emphasis to date has been upon development of an understanding of morphologies displayed under conditions of steady-state growth. For cellular growth morphologies it is found that experimental conditions which intensify the constitutionally-supercooled region lead to deeper, wider cellular grooves and cellular caps with smaller radii of curvature. The additional effects of imposed electrical fields have been selected for special consideration. Experiments have been designed and performed to isolate the field-induced effects of electromigration and non-uniform Joule heating at the interface. Statistical analysis of collected data and development of a model is in progress.

An understanding of structural inhomogeneities as they occur under conditions of non-planar, non-steady-state advance in real castings is clearly of technological interest. Consequently, a shift in the focus of the work to
Thermochemistry of Cadmium (Neuendorf and Spitzer)

The thermochemistry of cadmium and its compounds is of interest in connection with a study of cadmium as a trace atmospheric pollutant. The temperatures at which the metal and its compounds have significant vapor or decomposition pressures are exceeded in a number of important industrial processes whose streams contain cadmium compounds in various forms and concentrations.

Thermodynamic data obtained from the literature have been employed to plot the ranges of thermodynamic stability for cadmium compounds in the Cd-O-C-S system as a function of gas compositions and temperatures expected in industrial processes. This information is employed to predict which compounds are thermodynamically possible to form and which compound is ultimately stable when a specified cadmium-containing material is subjected to a specified environment.

Thermogravimetric experiments were undertaken to determine the products of thermal decomposition when cadmium metal, cadmium compounds, and complex cadmium-containing materials are exposed to controlled thermal and gaseous environments.

Certain industrial processes have been selected for investigation as potential sources for cadmium emission to the environment. On-site samples have been collected from industrial process streams in an effort to construct trace-metal material balances for the processes. The thermodynamic and thermogravimetric data are utilized to deduce cadmium-release mechanisms and to design sampling strategies.

Support: NSF (RANN GI35106)
metallic surfaces yield information about the nature of the film and allow evaluation of the corrosion behavior of alloys.

A major fraction of this research effort was devoted to the development and construction of electrochemical cells, circuitry, and techniques for anodic potentiostatic polarization. The potentiostatic method is used to construct polarization curves showing the dependence of current on potential. The potential is held constant or varied at some controlled rate with the current allowed to reach a steady-state value. Over a certain range of potentiostatically-imposed anodic potentials, there may exist a passive state characterized by a low, constant current due to protective film formation. If this passive state can be stabilized by proper selection of alloy composition, good corrosion resistance should be achieved.

The anodic behavior of most pure metals, including iron, nickel, and copper, is well known. However, the contribution of individual alloying elements to the anodic behavior exhibited by alloys is not well understood. This study examined the passive anodic behavior exhibited by a low-carbon, age-hardenable steel containing nickel, columbium, and copper and compared the polarization curves to those obtained for the pure elements in an attempt to deduce the contributions of the alloying elements, individually or synergistically, to the observed behavior. The behavior of the experimental alloy in 1 N H$_2$SO$_4$ was similar to that of Cr-Ni stainless steel.

**Support:** Inland Steel-Ryerson Foundation (fellowship)  
Union Carbide Corporation

**M.S. Thesis:**  
Corrosion Resistance of Stainless Steels in Chloride-Containing Media (Taylor, Spitzer, Tobin)

Aqueous corrosion resistance of stainless steels is adversely affected when the environment contains chloride ions. The stability of the passive film on the metal surface is destroyed and pits are produced. Certain solute elements are known to reduce susceptibility to pitting by rendering the passive state more stable.

The goal of this project (newly initiated, 9/73) is to understand the mechanisms responsible for pitting attack and the role of alloying elements in the passive film. Such understanding is expected to lead to the design of alloys having improved corrosion resistance in marine environments.

Surface studies of experimental alloys, which have been subjected to controlled corrosive environments in a potentiostatic cell, will permit correlation of film structure and composition with electrochemical behavior. Apparatus and techniques for potentiostatic-polarization measurements have been developed in an earlier project. Instrumental techniques for surface analysis which are available as central facilities include: electron spectroscopy for chemical analysis (ESCA), Auger electron spectroscopy (AES), and scanning electron microscopy (SEM). For example, ion sputtering combined with ESCA analysis will provide composition-depth profiles. Thus, any enrichment of alloy components in the surface layers will be detected.

Support: NSF-MRL GH33574
Inland Steel-Ryerson Foundation (fellowship)
Objectives: The purpose of this research is to gain improved understanding on a macroscopic level of the thermal effects and solute or impurity redistribution during crystal growth.

Approach: The approach involves the dynamic measurement of temperature and concentration distributions using optical techniques. The Mach-Zehnder interferometer used for monitoring the concentration has the advantage of continuous observation without disrupting the process of solidification and does not appear to have been used in any previous crystal growth studies. For an initial solidification test, NaCl-H$_2$O solutions were studied. The choice of the melt was primarily dictated by the availability of the spectral index of refracted data which were needed to interpret the Mach-Zehnder interferograms.

Progress: Sodium chloride-water solutions with concentrations ranging from 0.25 to 4.0 molar were used in the experimental tests under different thermal conditions. Analysis has been performed to predict the transient one-dimensional solidification and solute redistribution processes occurring during freezing of the solution. The measured solid-liquid interface position, temperature, and concentration distribution data were then used to establish the validity of the analytical model. From the comparison of experimental data with the theoretical predictions, it is concluded that the analytical model simulates accurately the solidification of solu-
tions. It was found that the common approximation of a constant distribution coefficient during solidification processes in a finite region is invalid. The interferometer was found to be a powerful diagnostic tool for measuring temperature and/or concentration distributions during growth of semitransparent crystals. The detailed results and conclusions of this phase of the research will be described in the dissertation by B. W. Grange which is under preparation.

Support: ARPA-IDL
NSF-MRL

Publications:


Talks:


Staff Members:
Raymond E. Taylor
Associate Senior Researcher
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Associate Senior Researcher
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K. Y. Wu
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Evaluation of Flash Diffusivity Methods (Taylor, Clark)

The flash diffusivity method is used to generate over 3/4 of the present thermal diffusivity data. This program has as its objective the critical evaluation of the method and the quantitative determination of the limitation and accuracy. The apparatus has been built and used to generate data on standard materials. Quantitative assessments have been made for many of the most important errors. The applicability of the method has been widened to include non-destructive testing of large artifacts.

Support: NSF Grant GK 23247

Thermal Transport in Carbides (Taylor)

The quantitative determination of the mechanisms influencing energy transport in transition metal carbides must be understood before these materials can be effectively utilized in high temperature applications. During the first year of this
grant, a cooperative venture was launched with qualified and interested personnel at the University of Illinois (Dr. W. Williams), University of Connecticut (Dr. P. Klemmens) and Los Alamos Scientific Laboratory (Dr. E. Storm and Dr. P. Wagner). Dr. Storm provided a series of samples of Zr C\textsubscript{x} which were measured at TPRC. The results showed a strong dependence of the thermal conductivity on the carbon vacancy concentration near stoichiometry. This behavior is being examined in detail.

Support: AFOSR Grant -72-2375

Thermal Transport in Transition Metal Carbides, Borides and Nitrides (Taylor, Wu, Touloukian)

This project investigated certain aspects of energy transport in transition metal carbides, borides and nitrides to provide preliminary basis for a large effort (see Thermal Transport in Carbides, AFOSR Grant 72-2375). The separation of the electronic and lattice components of the thermal conductivity was accomplished, on at least a semi-quantitative basis, using the alloy method to determine the Wiedemann-Franz-Lorenz number (L). It was shown that the value of L increases above the classical value (L\textsubscript{o}) above room temperature.

Support: NSF - MRL

Publications:


Talks:
Use of Silicon Schottky Barriers as GEISHA Targets (Thompson and Namordi)

Large area (1.27 mm²) Al–nSi Schottky barrier junctions have been fabricated in unpassivated, SiO₂ passivated and Al₂O₃ passivated structures. Guard rings surround the active area and lead to breakdown voltages as high as 200 volts.

The current gain of Schottky barrier targets was measured over a wide range of Al thicknesses and with electron beam energies of 1-30 keV. It was determined that the energy required to create a hole-electron pair is 3.44 ± 0.2 eV. Under pulse-mode dynamic testing, output pulses of 13.1 A are obtained with rise and fall times of 0.72 nsec into a 10 A (optimum) load. The amplifier pulse-mode efficiency is 85%, the low-pass bandwidth is 875 MHz
and the \( P^2 \) figure is 82W-GHz\(^2 \). In addition, we have achieved small signal transconductance and power gains of 4.35 mhos and 40 db.

This work is now completed.


Properties of \( \text{Al}_2\text{O}_3 \) as an Insulator on Elemental and Compound Semiconductors

(Thompson, Munro, Ohm, Donley)

The objective of this work is to deposit \( \text{Al}_2\text{O}_3 \) by electron-gun evaporation onto clean surfaces of elemental and compound semiconductors. The films so deposited have a relative dielectric constant of about 8.0, a refractive index of 1.61 and a breakdown field strength exceeding \( 3(10^6)v/cm. \)

Quasistatic and high frequency measurements of interface-state densities show good agreement for samples of .04\( \mu \)cm pGe and .12 \( \mu \)cm nGe. Minimum surface state densities obtained to date are in the mid -10\(^{12} \) states/cm\(^2\)-eV. Surface state densities for Ge are minimum near mid-gap and increase sharply a few k\( T \) from the center.

\( \text{Al}_2\text{O}_3 \) on Si gives surface state densities in the low 10\(^{11} \) states/cm-eV range and exhibits excellent stability. \( \text{Al}_2\text{O}_3 \) on (111) GaAs surfaces shows high surface state densities \( (>10^{12}) \) but does provide some modulation. FET devices are to be fabricated in Ge and Si to evaluate performance under dynamic conditions.

Support: ARPA/NSF-MRL Contract No. GH33574
This project has the objective of investigating the metallographic and structural features of Al$_2$O$_3$ films deposited by electron beam techniques on semiconductor substrates including Si and Ge for FET applications. In order to evaluate the process parameters that would result in high yields and repeatable results for the oxide films, the films are studied with the aid of scanning electron microscope and x-ray techniques to characterize their microstructural features as well as their physical integrity with the substrates. Preliminary SEM studies of the films deposited on Si have shown that a wide variety of physical features like porosity, local separation of the film from the substrate, and localized phosphorus enrichment at the substrate can arise under unfavorable conditions of substrate preparation, film deposition and result in poor yields and failures of devices.

Another parameter that can affect the yield is encountered during the annealing step of the insulator with Al metal counterelectrodes placed on its surface. During the anneal, the migration of Al may occur through the insulator layer by bulk or grain boundary diffusion processes. Hence, diffusion studies of annealed films are also planned with the aid of SEM and electron microprobe.

Support: NSF-MRL GH33574
High Power Switching using Solid State Devices (Thompson, Miller, Myers, Reed, and Himelick)

This project is to develop solid state devices capable of switching high currents at high voltages with short "switch-open" times. Current levels of 1000 A are to be switched with off-state voltages approaching 100 kV.

Two methods are now being investigated. The first makes use of a corbino-disk structure with \( I_{NS} \) as the active material. The \( I_{NS} \) disk is inserted into a coil drivers by a pulse forming network which produces a large magnetic field for a short period of time. Interaction of the field and carriers should produce resistance increases of three orders of magnitude when the disk is operated at 78°C.

The second approach is utilization of optical/electron-beam input to maintain bulk semiconductor in a low-resistance conducting state until the excitation is removed. Turn-off times in the low microsecond range are experienced. Electron beam excitation is being investigated because of its higher efficiency by comparison with basic input.

Support: Air Force Systems Command; Contract No. F33615-72-C-2097

Semiconductor Device Modeling for Failure Prediction (Leon, Neudeck, Thompson, Razouk, and Kriegel)

It is desirable to predict failure mode and level for device/integrated circuit failure under conditions of high voltage spikes encountered in some environments. The failure mode is basically thermal-related and can occur at the junction (avalanche breakdown, second breakdown, or thermal burn-out) or in the metallization (melting of conductive
and subsequent open circuit). A model is being developed which would make use of minimal device/circuit data for modeling the failure modes. Such a model will permit design using large-scale computer programs (such as SEPTRE) to account for failure modes.

Support: RADC-F30602-72-C-0438

Publications:

Talks:

Ph.D. Thesis:

The principal objective of this program is to generate critical tables of standard reference data on the electronic properties of materials. The availability of adequate standard reference data tables is essential to the national progress, economy, and defense.

In each of the reference data generation projects, the first phase of work is data compilation. In the second phase, the compiled data are critically evaluated, analyzed, and synthesized, and recommended reference values are generated. The search of data is accomplished with the aid of our Electronic Properties Information Center (EPIC)'s Scientific Documentation which provides comprehensive and authoritative source information on the electronic properties (including also electrical, magnetic, and optical properties) of all matter through a continuing and systematic effort in thorough search, acquisition, review, codification, classification, and organization of all the existing information in the world literature on the electronic, electrical, magnetic, and optical properties and in putting this enormous amount of information into a mechanized and computerized information storage and retrieval system (this activity is not reported here).

After the existing data and information are compiled and organized, these are then critically evaluated regarding their validity and accuracy, the disagreements in conflicting data are resolved and reconciled, the data are correlated in terms of various controlling parameters and compared with theoretical predictions, etc. so as to generate recommended reference values. Besides critical evaluation and analysis of the existing data, theoretical methods and semiempirical techniques are employed to fill gaps and to extrapolate existing data so that the resulting recommended reference values are internally consistent and cover as wide a range of each of controlling parameters as possible.
The properties and materials covered in the current program are:

(1) Electrical resistivity - Elements
(2) Optical constants (absorption index and refractive index) - Alkali halides
(3) Hall coefficients - Elements
(4) Mobility - Elements
(5) Thermoelectric power - Elements

Support: Defense Supply Agency

Publications:


Transport in a Magnetic Field (Van Zandt and D. T. Dwyer)

The equations for charge transport by interacting carriers in a magnetic field have been rederived and found to have the same forms at long wavelengths and strong fields. The new derivation opens the possibility of a field dependent generalization of strictly antisymmetric statistics for electrons. The predictions of this generalization are being checked against the spectrum of atomic Helium; the work is nearly complete. Dwyer is presently writing his thesis in absentia.

Support: National Science Foundation - Materials Research Laboratory Contract GH 33574

Electronic Structure of \((\text{Ti, V})_{2.3}\) (Van Zandt)

A reasonable arrangement of energy bands and impurity states has been proposed for V doped Ti\(_2\)O\(_3\) within the context of a three dimensional model which satisfactorily accounts for the low temperature anomalies in the specific heat and is consistent with all other data on the system currently available. The model has been published in a recent Physical Review Letters. The model also predicts interesting anomalies and magnetic field dependences in the specific heat and magnetization density of the system. These predictions have been submitted for publication also.

Support: National Science Foundation - Materials Research Laboratory Contract GH 33574

Cyclotron Resonance Lineshape (Van Zandt and Rao)

A quantum mechanical theory of the line shape of cyclotron resonance has been developed. The theory uses a fully microscopic description of electron scattering off point impurities to determine the energy loss rate from the cyclotron motion. We expect strong frequency dependence of the effective relaxation time here for the first time derived, rather than assumed. The work should be ready for publication sometime this semester.

Support: National Science Foundation - Materials Research Laboratory Contract GH 33574
Publications:


Conduction Mechanisms in Thick Film Microcircuits (Deputy, Miller, Prabhu, Vest, and Fuller)

Studies of the resistance of RuO$_2$-glass resistors during firing and studies of the surface tension of the glass as a function of temperature were conducted. The results are consistent with the predictions of the theoretical model developed to describe the formation of resistor microstructure.

Studies of the removal of the ethyl cellulose-butyl carbilol screening agent led to the conclusion that the last traces of organic materials cannot be removed below 500°C. These results have led to a program to develop more suitable screening agents.

Investigation of the drying of RuO$_2$•X H$_2$O employing DTA and TGA techniques led to the development of a procedure for preparing anhydrous RuO$_2$ with the proper particle size range.

The solubility of RuO$_2$ in 63% PBO-25% B$_2$O$_3$-12% SiO$_2$ glass was determined as a function of temperature, both for the equilibrium case and for times typically associated with thick film resistor firing. A dependence of the solubility on particle size was observed.
Studies with the hot stage metallograph have shown the release of gas bubbles from resistors for unexpectedly long periods of time at normal firing temperatures. The source of the escaping gas is unknown at the present, but the phenomenon has far reaching implications as regards the microstructure development model.

It was demonstrated that no new crystal phases are formed during a normal resistor firing profile, but that crystalline phases originating from an interaction between the glass and the alumina substrate are formed during extended firing periods.

Resistor firing studies have demonstrated that the microstructure formation can be successfully slowed by lower temperature operation while still developing the identical ultimate structure; this work allows the structure to be quenched at various stages of development for subsequent analysis.

Studies of resistance during the microstructure development process have led to the conclusion that two different charge transport mechanisms may occur during the firing sequence, and that the relative contributions of these two mechanisms depend upon the particle size and particle size distribution of the conductive phase, as well as the degree of dispersion of the formulation.

Support: ARPA Grant No. DAHC15-70-G7  
Basil S. Turner Foundation  
DELCO ELECTRONICS DIVISION/GMC

Highly Conducting Oxides (Haws, Loeffler, Zeman and Vest)

Single crystal and polycrystalline samples of LaTiO$_3$, SmTiO$_3$, and GdTiO$_3$ have been prepared in varying rare earth titanium stoichiometries, in addition to polycrystalline samples of solid solutions in the GdTiO$_3$-LaTiO$_3$ system. Electrical resistivities have been measured from 4.2$^\circ$K to 1400$^\circ$K Hall co-
efficients and thermoelectric power measurements have also been made over most of the temperature range. The resistivity of LaTiO$_3$ exhibits metallic behavior over the entire temperature range, increasing linearly with increasing temperature to a room temperature value of approximately 9 milliohm-cm. The thermoelectric power of LaTiO$_3$ also increases linearly with increasing temperature to a room temperature value of -12 microvolts/°C. The resistivity of GdTiO$_3$ exhibits semiconducting behavior over the entire temperature range, with a room temperature value of approximately 300 ohm-cm and an activation energy of approximately 0.1 ev. The resistivity of SmTiO$_3$ exhibits semiconducting behavior for temperatures greater than 100°K, with a room temperature resistivity of approximately 200 ohm-cm, and an activation energy of approximately .08 ev. Below 100°K SmTiO$_3$ exhibits a resistivity which decreases with decreasing temperatures.

Single crystal X-ray data for all of the rare earth titanates confirmed that they are iso-structural with GdFeO$_3$ (space group Pnma) with lattice parameters as given in the following table:

<table>
<thead>
<tr>
<th>Compound</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>GdTiO$_3$</td>
<td>5.668</td>
<td>7.690</td>
<td>5.403</td>
</tr>
<tr>
<td>SmTiO$_3$</td>
<td>5.652</td>
<td>7.732</td>
<td>5.459</td>
</tr>
<tr>
<td>LaTiO$_3$</td>
<td>5.584</td>
<td>7.897</td>
<td>5.584</td>
</tr>
</tbody>
</table>

Studies with solid solutions in the LaTiO$_3$-GdTiO$_3$ system have been completed for the 75%, 50%, and 25% solid solutions, in addition to
the end members. All solid solutions indicate semiconducting behavior with activation energies decreasing with increasing lanthanum content.

Studies of solid solutions between various c-type cubic sesquioxides have been initiated. The two systems considered to-date are $\text{Tl}_2\text{O}_3$-$\text{Er}_2\text{O}_3$, and $\text{In}_2\text{O}_3$-$\text{Y}_2\text{O}_3$. Solid solutions containing 30, 60 and 80 atomic percent $\text{Tl}_2\text{O}_3$ or $\text{In}_2\text{O}_3$ have been prepared by coprecipitation techniques. Crystallographic studies, as well as studies of electrical properties, are in progress.

Support: NSF-MRL

Publications:


Talks:


M.S. Theses:
None

During the period since our previous progress report (1972) we have been principally concerned with the application of X-ray photoelectron spectroscopy to a study of the bulk structures of inorganic phases containing transition metal ions in low oxidation states. In addition to helping to elucidate the electronic and molecular structures of these materials, such studies are considered an important preliminary step in our utilization of this technique in the investigation of the changes which occur on the surfaces of heterogeneous catalysts.

Rhodium $3d_{3/2}$ and $3d_{5/2}$ core electron binding energies have been recorded for a series of complexes containing rhodium in the formal oxidation states $+3$, $+2$ and $+1$. These binding energies generally decrease in the order Rh(III) > Rh(II) > Rh(I), the trend which is expected from a simple point charge model. However, this interpretation does not take account of changes in co-ordination number and ligands, and in fact the rhodium(III) complex $\text{RhClI(CH}_3\text{)}(\text{PPh}_3)_2\text{CH}_3\text{I}$, obtained by the oxidative addition of methyl iodide to $\text{RhCl}_3\text{PPh}_3$, has a similar rhodium $3d_{5/2}$ binding energy to that of dimeric rhodium(II) acetate and its derivatives.
Thus unless comparisons are made between structurally related species in similar ligand environments, then an unambiguous correlation between binding energies and formal oxidation state should not necessarily be expected.

Within the series of rhodium(III) complexes several trends are apparent. One of the problems of relating binding energies between ionic and nonionic species is the unknown variations in Madelung type potential. For this reason we chose to internally reference the rhodium 3d_{5/2} binding energies of the chloro-complexes with respect to the related chlorine 2p_{3/2} binding energies, and to consider the energy difference $E_b[Rh(3d_{5/2}^-\text{Cl}) - Cl(2p_{3/2})]$ as a measure of binding energy changes occurring at the metal core. From this data it was found that there is invariably a clear distinction between the nitrogen donor complexes and those with sulphur and/or phosphorus donors. The former exhibit higher rhodium 3d_{5/2} binding energies, and the trend N > P = S is in keeping with the polarizability differences between the N, P and S donor atoms. A related trend in binding energies with change in ligand polarizability is also seen within the series of complexes RhX_3,3thiox (thiox = 1,4-thioxane), the 3d_{5/2} binding energies following the sequence Cl > Br > I. The complex RhClI(CH_3)(PPh_3)_2CH_3I, which contains the strong -CH_3 σ-donor, in addition to iodine and phosphorus donors, as expected has the lowest 3d_{5/2} binding energy of the rhodium(III) complexes.

We have also investigated the X-ray photoelectron spectra of rhodium(II) acetate Rh_2(0_2CCH_3)_4 and its derivatives of the type Rh_2(0_2CCH_3)_4,2L to establish whether rhodium core binding energies would reflect the different donor strengths of the ligands triphenylphosphine, thiourea, dimethylsulfoxide and pyridine. The relative insensitivity of the rhodium 3d_{5/2} binding
energy to these ligand changes precluded any such ranking of donor properties, and probably reflects their weak interaction with the Lewis acid rhodium(II) acetate.

It is now well established that for a particular stereochemistry, metal-halogen vibrational stretching frequencies generally increase with increase in oxidation state. Since metal core binding energies reflect the charge distribution at a metal centre, it is reasonable to anticipate a correlation between these binding energies and the appropriate metal-ligand stretching vibrations. Using data from the literature for the highest frequency infra-red active $\nu$(Rh-Cl) modes of the rhodium chloride complexes which we studied, we find that such a correlation exists. Increase in rhodium $3d_{5/2}$ binding energies parallel an increase in $\nu$(Rh-Cl). These correlations depend upon the co-ordination number (four for the complexes of rhodium(I) and (II), and six for the rhodium(III) species) and in the case of the rhodium(III) complexes upon the nature of the ligand atoms.

We have investigated the X-ray photoelectron spectra of a series of complex halides of rhenium of the types $\text{ReX}_6^{2-}$, $[\text{ReX}_5^-,L]^-$, $\text{Re}_2\text{X}_8^{2-}$ and $\text{Re}_2\text{Cl}_9^{2-}$. The purpose of this study was as follows: (1) To determine the binding energies of the metal core electrons in a series of complexes of relatively simple structure containing only one type of ligand atom, namely chlorine. (2) To study the effect of changing the halogen within the series $\text{ReX}_6^{2-}$, and changing the nature of the ligand molecule L in $[\text{ReCl}_5^-,L]^-$, on these same binding energies. (3) To determine the influence of the cation within a series of $\text{ReCl}_6^{2-}$ and $\text{Re}_2\text{Cl}_8^{2-}$ salts upon the metal core binding energies, and establish whether "cation effects" can be compensated for.
For the group of chloro-complexes which were studied, the rhenium $4f_{7/2}$ energies occur over the relatively narrow range of 43.8 to 42.4 eV and reveal no clear dependence upon formal oxidation state i.e. Re(IV) in ReCl$_6^{2-}$, [ReCl$_5$L]$^-$ and [Re$_2$Cl$_9$]$^-$, Re(IV,III) in [Re$_2$Cl$_9$]$^{2-}$ and Re(III) in [Re$_2$Cl$_6$]$^{2-}$. Within the series of complexes K$_2$ReX$_6$ (X = Cl, Br, I), the rhenium $4f_{7/2}$ binding energies decrease in the order Cl > Br > I, as expected from a consideration of ligand electronegativities.

Since these binding energies were measured on species containing different cations, differences in Madelung potential may well render detailed comparisons unrewarding. On the other hand, for these relatively simple anions it is reasonable to anticipate that changes in metal oxidation state will cause greater changes in the rhenium $4f_{7/2}$ binding energies than in the related chlorine $2p_{3/2}$ energies. Accordingly, if we now reference the $4f_{7/2}$ levels to some convenient value for the chlorine $2p_{3/2}$ level, say 198.0 eV, this procedure should provide a more meaningful guide to the metal oxidation state. These adjusted rhenium $4f_{7/2}$ binding energies show that the rhenium(III) derivatives do indeed have slightly smaller $4f_{7/2}$ binding energies than the rhenium(IV) complexes. Furthermore, by referencing the rhenium $4f_{7/2}$ binding energies to a standard chlorine $2p_{3/2}$ value, it is apparent that within each series of anions these energies are essentially identical, so that differences between the 'uncorrected' data, e.g. K$_2$ReCl$_6$ (43.5 eV) and [pyH]$_2$ReCl$_6$ (43.0 eV), are almost certainly due to small variations in Madelung potential. Also, for the salts [ReCl$_5$L]$^-$, it is clear that the rhenium $4f_{7/2}$ binding energies are not sensitive to the nature of L, a result in keeping with our studies on the rhodium(II) acetate derivatives Rh$_2$(O$_2$CCH$_3$)$_4$2L, in which we observed an insensitivity of the rhodium $3d_{5/2}$ binding energies
to variations in the ligand donor strengths.

Support: National Science Foundation (MRL Program GH33574)


Studies of the chlorine 2p binding energies of metal chloride clusters such as $\left[ Mo_6Cl_8 \right]Cl_4$ have now been completed. Results for these model systems will hopefully help us to interpret the changes which occur at the surfaces of active metal halide catalysts. For $\left[ Mo_6Cl_8 \right]Cl_4$ and its derivatives, we were able to detect the presence of two or three structurally different chlorine environments. Chlorine 2p binding energies for chlorine atoms in intracluster molybdenum-chlorine bridges ($Cl_b$), inter-cluster molybdenum-chlorine bridges ($Cl_b^\prime$), and terminal molybdenum-chlorine bonds ($Cl_t$) have been distinguished and are found to occur over a range of 2.4 eV. The binding energy order $Cl_b > Cl_b^\prime > Cl_t$ is followed and the surprisingly large differences in binding energy between these chlorine environments should enable such sites to be distinguished in phases of unknown structure. The results of the above investigations are currently being prepared for publication.

The X-ray photoelectron spectra of ten compounds of scandium(III) have been investigated and scandium 2p and oxygen 1s binding energies measured. Spectra were recorded with samples exposed to a 'zero' volt electron flux to reduce to a minimum any surface charging effects. This particular experimental procedure is extremely important in helping to unravel surface changes which accompany heterogeneous catalysis. The scandium 2p binding energies have been found to be relatively insensitive to the
environment about the central scandium atoms. In the case of Sc$_2$O$_3$ and Sc$_2$(C$_2$O$_4$)$_3$.6H$_2$O, 'satellite' peaks were observed on the high binding energy side of the scandium 2p doublets. These 'satellites' were fairly sharp and well defined in the spectrum of Sc$_2$O$_3$, being at ~11.3 and ~15.0 eV above the scandium 2p$_{3/2}$ peak. Our observations contrast with the results of other workers who claimed that such 'satellites' should not be observed for metal ions of the first transition series which possess d$^0$ electronic configurations. Since these 'satellites' cannot arise from 3d + 4s transitions, an assignment which has usually been favored for related peaks in the metal 2p binding energy spectra of paramagnetic metal ions of the first transition series, an alternative explanation is clearly necessary. At the present time the most attractive possibility is in terms of a monopole charge transfer transition (ligand + metal 3d). Related studies on TiO$_2$ and V$_2$O$_5$ have also revealed the presence of 'satellites' to the high binding energy side of Ti(2p) and V(2p).

Support: National Science Foundation (MRL Program GH33574)

Publications:
The following articles have resulted from work described in the 1972 and 1973 progress reports.


"The X-Ray Photoelectron Spectra of Inorganic Molecules. Part VI. Compounds Containing Rhenium-Oxygen and Rhenium-Halogen Bonds: Rhenium 4f, Chlorine 2p and Oxygen 1s Binding Energies and Their Correlation with


Talks:


Ph.D. Thesis:

"Crystallographic and Reactivity Studies on Halide Complexes of Rhenium(III) and Rhenium(IV) with 1,2-Bis(Diphenylphosphino)ethane," John A. Jaecker, December, 1973.
Properties of Martensite due to its Point Defect Content (Hall, Veeraraghaven)

An x-ray diffractometer adapted for single crystal work has been used to study small tetragonality in iron-nickel-titanium and in iron-nickel-carbon martensite. It allows independent measurement of the 002 and the 200, 020 peaks in martensite formed from single austenite crystals.

In iron-nickel-titanium alloys martensite tetragonality is due to non-random arrangements of solute atoms. A specially constructed high-vacuum, liquid-metal quenching apparatus produces quenching rates of $10^5^\circ\text{C}$ per second in single crystal slices. The resulting austenite is free of x-ray satellite peaks which are known to indicate TiNi$_3$ clusters. Subsequent aging of the austenite produces satellites as expected. We can now measure the tetragonality of martensite in the initial stages of NiTi$_3$ cluster formation. Measurements will be made for titanium levels up to 7 atomic percent.

In iron-nickel carbon martensite the positions of 200, 020 and 002 peaks of ferrous martensite have been measured individually by a precision x-ray diffractometer technique. Martensite with 18% Ni and 0.1, 0.2, 0.3, and 0.4 wt% C was formed by salt-water quenching from preoriented austenite single-crystal slices about 0.5 mm thick. The variations in x-ray peak positions interpreted as changes in lattice parameter yield to the first approximation:

\[
\frac{\Delta a}{a_0} = -0.005 \text{ [wt\% C]} \\
\frac{\Delta b}{a_0} = -0.016 \text{ [wt\% C]} \\
\frac{\Delta c}{a_0} = 0.037 \text{ [wt\% C]}
\]
or carbon contents between 0.1 and 0.4. For such carbon contents the martensite has packet or mixed packet-lenticular morphology; consequently, this martensite is not cubic as is sometimes claimed but in orthorhombic. The significance of the inequality of $a$ and $b$ is unclear. In an attempt to shed light on that inequality, the peaks of tempered martensite are being studied for carbon contents of 0.0, 0.8, and 0.8% by weight. Results show that the axial ratios approach unity during tempering but that significant deviations from cubic symmetry are present after tempering for 15 min. at 400°C in carbon bearing alloys.

Support: NSF GH33574, GH40440

Dislocation Arrangements in Concentration Gradients (Boah)

The dislocation configurations developed in nickel single crystals as a result of diffusion of carbon from a vapor source were studied experimentally. Carbon was diffused for 30 min. at 1000°C into the (111) surfaces of thick nickel crystals, and the resulting dislocation arrangements in the diffusion zone were examined by etch pitting (111) sections. The dislocation density increased from the "grown-in" $1.5 \times 10^6$ per cm$^2$ but in other regions near that surface it was about $10^7$ per cm$^2$. At least half of all the dislocations appeared to be arrayed in subgrain boundaries in these sections. The dislocation density decreased towards the interior until at about $3.5 \sqrt{D_t} \ (\sqrt{D_t} = 210 \ \mu m)$ it approximated the "grown-in" dislocation density, but even at distances exceeding $0.7 \sqrt{D_t}$ there still exist locally high density regions. These have a regular geometry in which dislocations appear to be on (111), (111), or (111) slip planes. The subgrain size was 36 \mu m near the as-diffused surface and increased, until at $3.5 \sqrt{D_t}$, it was 160 \mu m, which was the average subgrain size in the undiffused crystal.
Modulated Microstructure Heat Treatable Alloy Steel (Chen)

Alternating layers of hardened steel and ductile austenite have been produced using 01 (0.9% C, 1% Mn) steel for the hard layer and TC 30 steel (30% Ni, 0.1% C) as the soft layer. The layered specimen were produced by hot rolling in stainless steel jackets. Substantially complete bonding was obtained and by selective pre-oxidation the removal of the stainless jacket is facilitated. The technique of fabrication appears satisfactory and offers opportunity to form partially bonded layers.

In the preliminary samples, crack propagation proceeds from the brittle 01 layers through the soft layer without substantial deformation in the soft layer. The brittle behavior of the complex appears to be due to the triaxial tension developed in the fully bonded soft layer. A redesign of the complex to reduce the constraint is in process.

Support: ARPA DA 1573G12
Publications:


Talks:


Ph.D. Thesis:

Staff Member: Nicholas Winograd  Assistant Professor of Chemistry
Samuel J. Hruska  Associate Professor of Materials Engineering

Postdoctoral Research Associates: K.S. Kim

Graduate Research Students: W.A. Watkins  C.D. Sell
D.J. Pocker  J.S. Hammond
J.H. Cary  S.W. Gaarenstroom
D.H. Karweik  L.M. Fetterman
J.C. Holland  P. Frederick
D.V. Smith


The objective of this work has been to develop instrumental and theoretical aspects of reflection spectroscopy and ESCA as tools to aid in elucidating the mechanism of a variety of electrode reactions. The in situ optical properties of the electrified interface are investigated using transparent electrodes. The resulting optical data is then correlated to steady state electrode structure using ESCA as a probe to study surface chemical environment.

Thus far, we have studied Au, Pt and Pd electrodes which have been oxidized in acidic aqueous solution. We have, using ESCA to identify the presence of the oxides, conclusively characterized PtO and PtO$_2$ layers on anodized Pt films presenting the best spectroscopic evidence yet available for their existence. The thickness of these layers was estimated to be on the order of 10 Å. We are presently studying the optical reflection spectra of anodized Pt to confirm these results. On the anodized Pd-oxygen electrode we have observed PdO, PdO$_2$, Pd(OH)$_2$ or Pd(OH)$_4$ in much thicker (~50 Å) layers with PdO$_2$ forming at a potential lower than its equilibrium potential. This has been explained by the reaction of oxygen with corroded Pd. Similar studies on gold electrodes have successfully isolated AuO$_{ads}$ and Au$_2$O$_3$ surface species. We feel this general approach to analysis of electrode surfaces has been exceedingly valuable in understanding electron transfer processes. We expect future applications to greatly expand the scope of this plan bringing a new dimension to this field of study.

Support: AFOSR-72-2238
Adsorption of Ag, Cu, and Au on Re: LEED and Auger Spectroscopy (Hruska, Pocker, Smith)

The steady state adsorption of Ag, Cu and Au on polycrystalline Re foils with predominantly (0001) faces exposed has been studied. A system permitting near normal vapor incidence concurrent with Auger spectrometric adsorbate concentration measurement was employed. Adsorption ranged smoothly from about 0.005 to 1 monolayer coverage over temperature ranges of roughly 100, 350, 275$^\circ$K for Ag, Cu and Au respectively; further substrate cooling of 50 to 100$^\circ$K yielded bulk growth. The low coverage adsorption was reasonably described by the equation 

$$\theta = A R^Y \exp(Q_R/kT)$$

where $\theta$ = fractional surface coverage, $R$ = inpingent flux in layers/sec and $A$, $y$ and $Q_R$ are as given here.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>$y$</th>
<th>-log$_10 A$(sec$^Y$)</th>
<th>$Q_R$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>3</td>
<td>26.23</td>
<td>6.46</td>
</tr>
<tr>
<td>Cu</td>
<td>$\frac{1}{2}$</td>
<td>6.88</td>
<td>1.80</td>
</tr>
<tr>
<td>Au</td>
<td>$\frac{3}{2}$</td>
<td>11.24</td>
<td>4.15</td>
</tr>
</tbody>
</table>

Surface crowding and deviations from the above were pronounced for Au ($\theta \geq 0.1$), clearly present for Ag ($\theta \geq 0.5$) and absent from the Cu results. This, coupled with size estimates for the adsorbed atoms and the measured reaction orders ($y$ above) indicated stable adsorbed clusters of 3 atoms for Au, either 7 or 3 atoms for Ag and 1 atom for Cu. These factors also indicated predominantly dimer desorption for all three (Ag monomer desorption likely if adsorbed trimers stable).

Several other features, either prerequisite or peripheral to the primary effort were noted. (1) Four weak Re Auger peaks were detected at 57, 272, 364, and 416 eV. (2) Electron stimulated desorption (of Ag at least) was clearly detected under a defocussed 3 kV, 7 $\mu$A beam. (3) Peak-to-peak Auger signals (derivative spectrum) appeared to be quite proportional to adsorbate coverages of or below one true monolayer. (4) The capability of measuring equilibrium vapor pressures (for Ag and Cu at least) was demonstrated. (5) Sticking coefficients of or very near unity prevailed for all three adsorbates on clean room temperature foils. (6) Preferred adsorption on and saturation of exposed
(0001) Re faces was indicated for all three adsorbates (more strongly substantiated for Ag). And finally, (7), slight evidence of at least some solubility of Cu and Au in Re was observed.

Thin Film Diffusion Effects: In-Plane (Hruska, Watkins)

An experimental deposition technique was developed to model a thin film couple after the standard bulk diffusion sandwich couple. The initial region of mixing between the two sides of the thin couple was less than 2 microns.

An empirical conversion parameter, following the bulk procedures of Ziebold and Ogilivie, was determined for thin films of gold and silver between 500 and 2,000 Å. X-ray intensity data from the electron microprobe were converted, through use of the parameter, to units of mass concentration. Pure and alloy films of gold and silver exhibited linearity between the microprobe x-ray intensity and film thickness up to 2,000 Å. The maximum error in alloy film composition using the conversion parameter was shown to be 10 atomic % at 500 Å.

Thin film couples of pure silver and gold annealed above 500°C, and at 416°C for times greater than 72 hours, exhibited dewetting on the pure gold side. The dewetting of the gold film was shown to be in accord with Mullin's theory of grain boundary grooving. For Ag-Au couples annealed below 500°C a zone of porosity occurred, increasing with time and temperature of anneal, leading to film separation near the pure silver side of the original region of mixing. The porosity formation was similar to that reported by investigators of bulk sandwich couples of pure Au and pure Ag.

Incremental thin film couples with initial concentration differences of 20% did not exhibit the zone of porosity which again was in agreement with investigators using bulk couples with small concentration differences. The diffused concentration profiles were compared with numerical solutions of the initial profile. The numerical technique was based on an approximate solution to Fick's second law for one dimensional diffusion.

A series of apparent diffusion coefficients was determined for temperatures between 200 and 416°C. A plot of ln D versus 1/T was linear with a coefficient of correlation of 0.99. The data fit the following relationship

\[ D = 1.9 \times 10^{-7} \exp(-10,900/RT) \text{ cm}^2\text{sec}^{-1} \]
An apparent diffusion coefficient was also determined for a series of pure Ag and Au couples annealed at 416°C and compared favorably with the incremental couples' diffusion coefficient at the same temperature.

Two models were considered in order to attribute the apparent diffusivity to a single transport mechanism. The surface diffusion model was refuted because of the low reported value of activation energy (10.9 kcal/mole), in comparison with what was theoretically expected and experimentally reported by other investigators. A model attributing the apparent diffusivity to transport along the film's grain boundaries was considered to be likely, if the grain boundaries could be assumed in a high state of disorder.

Support: NSF-MRL

ESCA-AES-LEED Surface Studies (Kim, Frederick, Hruska and Winograd)

The major objective of this study is to characterize surface layers formed on clean metals using electron spectroscopy. The ESCA technique has been applied specifically to systems where changes in oxidation state of the metal are involved. The AES-LEED approach has been employed to characterize these systems when single crystal substrates are involved.

Exposure of a variety of metals to dry oxygen has allowed, using ESCA, the identification of several types of molecules generally classified as gross surface defect structures. For many of these systems, this direct spectroscopic evidence represents the first direct proof for their existence. For example, on Ni surfaces, NiO$_{ads}$ (chemisorbed oxygen atoms), NiO, Ni$_2$O$_3$, and NiO$_{ads}$ have been characterized and the interconversion of the forms has been studied as a function of temperature (−80°C to 300°C) and under ion ($O_2^+$ and Ar$^+$) bombardment. Results show that Ni$_2$O$_3$ is, below 100°C, a stable and predominant species within 40 Å of the surface of Ni metal exposed to 200 torr oxygen. High concentrations of Ni$_2$O$_3$ can also be prepared by $O_2^+$ ion bombardment at −80°C. These results have direct bearing on calculated band structures of NiO and on the behavior of NiO as a catalyst.

Similar studies on Cu, Pd, Ag Cd and Cr have indicated the presence of similar excess oxygen species. In all cases, we have observed the chemisorbed oxygen layer before formation of the phase oxide. In addition, the presence of
Cu$_2$O$_3$, AgO$_2$ and CdO$_2$ have been confirmed as stable surface species. Any interpretation of the surface chemistry of these materials must now include the above observations.

We have observed, for the first time, direct proof for a general solid state chemical reaction at solid-solid interfaces. For all systems studied to date we have confirmed that for the two metals A and B or their oxides AO and BO that for a region approximately 20 Å thick at the interface between AO and B:

\[
AO + B \rightarrow BO + A
\]

The degree of reaction is directly related to the value of $\Delta G^\circ$ for the process. The reaction proceeds at room temperature and is virtually instantaneous. We feel this result will have a direct bearing on understanding many thin film processes.

A future phase of this research deals with the interaction of CO with Fe (stabilized with Ni) single crystals. ESCA will be employed to measure changes in the 1s binding energies of adsorbed C and O on both 100 and 110 faces. AES will allow determination of the relative amounts of C and O under steady state adsorption-desorption conditions. LEED will be employed to disclose any structure developed in the adsorbate-substrate system.

Support: NSF-MRL

A Study of Lateral Diffusion in Thin Film Couples of Gold and Silver (Watkins and Hruska)

An experimental deposition technique was developed to model a thin film couple after the standard bulk diffusion sandwich couple. The initial region of mixing between the two sides of the thin film couple was less than 2 microns.

Thin film couples of pure silver and gold annealed above 500°C, and at 416°C for times greater than 72 hours, exhibited dewetting on the pure gold side. The dewetting of the gold film was shown to be in accord with Mullin's theory of grain boundary grooving. For Ag-Au couples annealed below 500°C a zone of porosity occurred, increasing with time and temperature of anneal, leading to film separation near the pure silver side of the original region of mixing. The porosity formation was similar to that reported by investigators of bulk
sandwich couples of pure Au and pure Ag.

Incremental thin film couples with initial concentration differences of 20 atom% did not exhibit the zone of porosity which again was in agreement with investigators using bulk couples with small concentration differences. The diffused concentration profiles were compared with numerical solutions of the initial profile. The numerical technique was based on an approximate solution to Fick's second law for one dimensional diffusion.

A series of apparent diffusion coefficients was determined for temperatures between 200 and 416°C. A plot of ln D versus 1/T was linear with a coefficient of correlation of 0.99. The data fit the following relationship

\[ D = 1.9 \times 10^{-7} \exp \left( -10,900/RT \right) \, \text{cm}^2 \text{sec}^{-1} \]

An apparent diffusion coefficient was also determined for a series of pure Ag and Au couples annealed at 416°C and compared favorably with the incremental couples' diffusion coefficient at the same temperature.

Two models were considered in order to attribute the apparent diffusivity to a single transport mechanism. The surface diffusion model was refuted because of the low reported value of activation energy (10.9 kcal/mole), in comparison with what was theoretically expected and experimentally reported by other investigators. A model attributing the apparent diffusivity to transport along the film's grain boundaries was considered to be likely, if the grain boundaries could be assumed in a high state of disorder.

Support: NSF-MRL

Publications:


Talks:


"ESCA and Metal Surfaces", presented by N. Winograd, Midwestern University Analytical Chemistry Conference, Columbus, Ohio, November 10 and 11, 1972.


"X-ray Photoelectron Spectroscopy of Metal Surfaces", presented by N. Winograd, Departmental Seminar, Bowling Green State University, Bowling Green, Ohio, February 9, 1973.


Ph.D. Theses:

APPENDIX A

PUBLICATIONS

Fundamentals of Vacuum Technology, a commercial, self-paced learning package employing a standard textbook, over 500 pages of supplemental notes and over 10 hours of video tape; designed and written by R. M. Anderson, copyright, Purdue University 1973.


"Observation of Impurity Conduction Associated with the L-Minima in N-GaSb(Se)," Ru-Yi Sun and W. M. Becker, S. S. Comm. (to be published).


"Sum and Difference Frequency Generation in Acoustoelectric Domains in GaAs, T. E. Parker and Ralph Bray, Phys. Lett., to be published.


"Coalescence of Helium Bubbles in Aluminum," K. Y. Chen and J. R. Cost, accepted for publication, J. of Nucl. Mat.


"Optical Study of Ion-Defect Clustering in CaF$_2$:Er$^{3+}$," F. K. Fong, J. B. Fenn, Jr., and J. C. Wright, to be published, J. Chem. Phys.


"Quantum Efficiency of Diffusion Limited Energy Transfer in La$_{1-x-y}$Ce$_x$Tb$_y$PCl$_3$-x-y," J. C. Bourcet and F. K. Fong, to be published, J. Chem. Phys.


"Ultrasonic Studies of Amorphous $\text{As}_2\text{S}_3$ and of a Protonic Semiconductor Through Its Glass Transition," D. Ng and R. J. Sladek, Proceedings of 5th International Conference on Amorphous and Liquid Semiconductors, Garmisch-Partenkirchen, W. Germany, September 3-8, 1973 (to be published).


APPENDIX B

M.S. THESIS


"A Spectroscopic Study of the Symmetries and Deformation-Potential Constants of Singly-Ionized Zinc in Germanium," F. Barra (deceased), to be awarded posthumously.


"Helicon Transmission and Helicon-Excited Paramagnetic Resonance in Hg\textsubscript{1-x}Mn\textsubscript{x}Te," R. T. Holm, October, 1973.


"Electrical and Raman Studies of Pure and V-doped Ti\textsubscript{2}O\textsubscript{3}," S. H. Shin, December, 1972.


"Crystallographic and Reactivity Studies on Halide Complexes of Rhenium(III) and Rhenium(IV) with 1,2-Bis(Diphenylphosphino)ethane," J. A. Jaecker, December, 1973.


APPENDIX C

Department of Chemistry

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