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ANNUAL TECHNICAL PROGRESS REPORT
for the Period
1 July 1966 to 30 June, 1967

Contract SD-68

31 August, 1967



MATERIALS SCIENCE CENTER
CORNELL UNIVERSITY
Ithaca, New York

196

Annual Technical Report
for the Period
1 July 1966 to 30 June 1967

submitted to the
Advanced Research Projects Agency

by the
Materials Science Center of Cornell University
Ithaca, New York

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I. INTRODUCTION

The Materials Science Center at Cornell University is a free association of professors interested in various aspects of materials science. It was founded in 1960 under the auspices of the Advanced Research Projects Agency with the objective of enhancing research and intensifying graduate training in this area with emphasis on the interdisciplinary character of modern materials investigations.

The present Technical Progress Report for 1966-1967 is intended to give a condensed account of the research activities of all the members of the Materials Science Center, their associates, and their graduate students. It consists of summaries prepared by the individual members of the research objectives and progress of their research during the year.

An Executive Committee decides on the policies of the Center and the selection and funding of the individual research projects and of the Technical Facilities maintained by the Center. In 1966-1967 the members of this committee were:

- R. W. Balluffi, Professor of Materials Science and Engineering
- S. M. Brown, Jr., Dean of the College of Arts and Sciences and Professor of Philosophy
- D. R. Corson, Provost
- D. B. Fitchen, Associate Professor of Physics
- J. L. Gregg, Professor of Materials Science and Engineering
- D. F. Holcomb, Director of the Laboratory of Atomic and Solid State Physics and Professor of Physics
- F. A. Long, Vice President for Research and Advanced Studies and Professor of Chemistry, Chairman
- G. H. Morrison, Professor of Chemistry
- H. S. Sack, Director of the Center and Walter S. Carpenter, Jr., Professor of Engineering
- A. Schultz, Jr., Dean of the College of Engineering and Professor of Industrial Engineering and Operations Research
- R. L. Sproull, Vice President for Academic Affairs and Professor of Physics
- W. J. Spry, Associate Director of the Center, Secretary
- W. W. Webb, Professor of Engineering Physics

During the year, the Center also benefited from the advice of an outside review committee, the Visiting Committee, whose members during 1966-1967 were:

- W. H. Armistead, Vice President for Research, Corning Glass Works
- J. E. Goldman, Director, Ford Scientific Laboratory
- N. B. Hannay, Executive Director, Research-Materials Division, Bell Telephone Laboratories
- C. L. McCabe, President, Koebel Diamond Tool Company
- A. S. Nowick, Professor, School of Mines, Columbia University
- C. S. Smith, Professor of Physics, Case Institute
- G. H. Vineyard, Associate Director, Brookhaven National Laboratory

II. RESEARCH REPORTS

On the following pages are presented the summaries of objectives and results of the research efforts of the individual members, arranged alphabetically according to the Principal Investigator. A member's total research program is subdivided into separate research projects, which form distinct units and can be characterized by more specific titles than is possible by uniting all of a professor's research projects under one single heading. These summaries contain the names of the research associates and research assistants associated with each project, as well as a list of publications* (published or accepted for publication during the report period) and theses submitted for Ph.D. or M.S. degrees conferred during the present academic year.

These summaries and lists of publications represent the total research efforts of the members of the Center in the area of materials research, irrespective of whether the main source of funding comes from ARPA or from other agencies. The main support for each individual research project is clearly indicated. However, all projects benefit to some degree from the ARPA funding of the Materials Science Center, through the use of space or central technical facilities provided by the Center.

ELECTRONIC AND VIBRONIC SPECTROSCOPY OF ORGANIC MOLECULES

A. C. Albrecht, Professor, Department of Chemistry

H. Sauter Research Associate

P. Berlow, R. Castonguay, D. Friedrich, P. Johnson, D. Matthews and
J. Tang Research Assistants

Objective

To understand the effect of nuclear motion on electronic properties of organic molecules such as transition moments, radiative and radiationless relaxation processes, Raman intensities.

Approach

Use of polarized photoselection techniques in rigid solution, polarized crystal spectroscopy, Stark effect studies, phase shift techniques for the study of relaxation phenomena, electroluminescence techniques, and theoretical studies based on variation-perturbation techniques.

Progress

The development of a Stark effect apparatus, as applied to vibronic states of organic molecules by Dr. Sauter, has reached a point where crucial tests of the effects are being made. Similarly, Mr. Berlow has constructed a phase shift apparatus and is making pilot studies on a rigid organic solution. Mr. Castonguay is completing studies on polarized phosphorescence in the chlorobenzenes. Many unusual effects have been found, including fluorescence enhancement with decreasing viscosity. Miss Tang has made considerable headway in the study of Raman intensity theory and is now engaged in the first computations of intensities using the hydrogen molecule ion as a starting point. She has already reproduced published calculations of polarizability using a valence type function. Mr. Johnson completed a study of the assignment of electronic states of the benzene radical; publication of this material is in process. The assignments verify predictions made by Valence-Bond Theory and completely disagree with those based on Molecular Orbit Theory.

PUBLICATIONS

"Electronic and Photochemical Properties of Carbon Dioxide Anion and Some Benzyl Type Radicals," P. M. Johnson, Ph.D. Thesis, Cornell University, February 1967.

This research is supported by the Advanced Research Projects Agency and the National Science Foundation

ELECTRONIC SPECTROSCOPY AND TWO PHOTON ADSORPTION

A. C. Albrecht, Professor, Department of Chemistry

J. Laposa

Research Associate

D. Kliger

Research Assistant

Objective

To study electronic states of organic molecules through two photon absorption, via either real or virtual states, and to detect previously unseen luminescences.

Approach

Use of Q-switched laser in conjunction with an intense xenon flash, a technique pioneered by Mahr and Fröhlich. Laser pulses "pump" short lived singlet states and xenon flashes can be used to detect their absorption spectroscopy. Ordinary virtual state spectroscopy can be explored also. Feeble luminescence is sought for after direct one photon excitation by laser using gated detection.

Progress

Progress has been very slow and difficult. No definitely positive results have been found except for the sighting of short lived triplet states. Nevertheless the numerous problems which have been encountered are being overcome one by one and the outlook is optimistic. Efforts to date have concentrated on the "pumping" version of the spectroscopy - one photon absorption by the laser - followed by xenon flash absorption spectroscopy. The detection has been strongly hindered by very bright sample luminescence. This appears to be the most difficult of the approaches and so will the detecting of feeble luminescences offer serious problems.

This research is supported by the Advanced Research Projects Agency, the National Science Foundation and the National Institutes of Health

PHOTOELECTRIC AND PHOTOCHEMICAL PROPERTIES OF ORGANIC SOLUTIONS AT VERY HIGH AND VERY LOW VISCOSITIES

A. C. Albrecht, Professor, Department of Chemistry

P. Kottis and J. Bullof

Research Associates

P. Beckowies, R. Ott, F. Schwarz, F. Douglas, P. Johnson, K. Cadogan
and H. Pilloff

Research Assistants

Objective

1) To understand the nature of the "solvated" electron, its mobility and the "trapped" electron (on chemical species) in both rigid and fluid systems.

2) To unravel primary photochemical processes which are isolated from secondary events at high viscosities.

Approach

Multiple beam photoconductometric, spectrophotometric techniques and ESR detection in both rigid and fluid organic solutions at different temperatures. Dispersion of organic crystallites are also studied.

Progress

1) P. Beckowies, a new student, is building a high vacuum system for degassing rigid solutions. This is to prepare solutions which have selected additives so that various trapped electron species may be created.

2) R. Ott is studying polarization currents in crystallites suspended in rigid organic solutions. He has succeeded in this for several aromatic molecules. He will emphasize temperature dependence of signals.

3) F. Schwarz is just beginning work on mechanism of radical formation in rigid solutions.

4) F. Douglas will pick up where H. Pilloff left off. The latter has been the first to show that photoionization in fluid solutions is biphotonic.

5) P. Johnson has completed his work and has demonstrated that CO_2 can act as an electron trap in rigid organic solution.

6) K. Cadogan has just left. He has shown that the triplet state serves as the intermediate in photoconductivity and that the ionization is triphotonic when two beams are used.

A. C. Albrecht

PUBLICATIONS

- "On the Biphotonic Mechanism of Benzyl Radical Formation in Rigid Organic Solutions," P. M. Johnson and A. C. Albrecht, J. Radiation Chem. (In Press).
- "Direct Measurement of A Biphotonic Photoionization in Liquid Solution," H. S. Pilloff and A. C. Albrecht, Nature 212, 499 (1966).
- "On Stimulated Recombination Luminescence in Rigid Amorphous Organic Solutions," A. C. Albrecht, P. M. Johnson and W. M. McClain, Proceedings of the Int. Conf. on Luminescence, Budapest, August (1966).
- "The Direct Measurement of a Biphotonic Photoionization in Liquid Solution and Some Studies on Electrical Conductivity in Low Dielectric Constant, Organic Solution," H. Pilloff, Ph.D. Thesis, Cornell University, February 1967.
- "Photooxidation in Rigid Media and Triplet-Triplet Absorption Spectra of Three Benzene Derivatives," K. D. Cadogan, Ph.D. Thesis, Cornell University, September 1966.

This research is supported by the Advanced Research Projects Agency, the National Science Foundation, and the National Institutes of Health.

THEORY OF CONDENSED MATTER

V. Ambegaokar, Associate Professor, Department of Physics

G. Eilenberger Research Associate

Objective

To study the ordered states of matter with emphasis on superconductors and superfluids.

Approach

This project is closely influenced by, and tries to predict, interesting experimental developments in the area described above.

Progress

(1) The theory of surface nucleation of superconductivity in strong coupling superconductors (like lead) has been worked out. The theory shows that the effects of strong coupling include a non-trivial renormalization factor, the inclusion of which makes for a quite satisfactory contact between the theory and experiments on the temperature dependence of the magnetic field at which nucleation is possible.

(2) A theory of the resistive transition in narrow superconducting channels has been worked out (J. S. Langer and V. Ambegaokar). This theory was provoked by recent experiments of Parks on this phenomenon. However the theory suggests that these experiments are probably not measuring an intrinsic effect, but are probably influenced by inhomogeneities in the experimental samples. New experiments to test the theory have been started at Cornell (under Professor W. W. Webb).

PUBLICATIONS

"Bulk (H_{c2}) and Surface (H_{c3}) Nucleation Fields of Strong-Coupling Superconducting Alloys," G. Eilenberger and V. Ambegaokar, Phys. Rev. 158, 332 (1967).

"On the Intrinsic Resistive Transition in Narrow Superconducting Channels," J. S. Langer and V. Ambegaokar, Phys. Rev. (in press).

"Ultrasonic Attenuation in Pure Strong Coupling Superconductors," V. Ambegaokar, Phys. Rev. Letters 16, 1047 (1967).

This research is supported by the Advanced Research Projects Agency and the Office of Naval Research

THEORETICAL SOLID STATE PHYSICS

N. W. Ashcroft, Assistant Professor, Department of Physics

D. C. Langreth Research Associate

J. Lawrence Research Assistant

Objective

To investigate the electronic structure of solid and liquid metals, and of their alloys.

Approach

The deduction of the fundamental electron-ion interaction from Fermi surface data leads to the Born Oppenheimer potential between ions. In turn this leads to the structure factor for pure metals and alloys, and to the lattice spectrum for solid metals.

Progress

The Fermi surface and band structure of In have been calculated; the derived transport properties are in good agreement with experiment. Ion-ion interactions have been obtained as a function of electron density. Transport properties of a number of binary liquid alloys have been calculated. The effects of pressure on Fermi surface structures have also been investigated.

PUBLICATIONS

- "Structure Factor and Direct Correlation Function for a Chemical Hard Sphere Fluid," N. W. Ashcroft and N. H. March, Proc. Roy. Soc. A297, 336 (1967).
- "Hard Core Dimensions of Noble Gas Atoms," N. W. Ashcroft, Physica 34 (1967).
- "Compressibility and Binding Energy of Simple Metals," N. W. Ashcroft and D. C. Langreth, Phys. Rev. (1967) (in press).
- "The Role of Volume Dependence in the Resistivity of a Liquid Metal," Physics Letters 23, 529 (1966).
- "Structure of Binary Liquid Mixtures: I," N. W. Ashcroft and D. C. Langreth, Phys. Rev. (1967) (in press).
- "Electron-ion Pseudopotentials in Metals," N. W. Ashcroft, Physics Letters 23, 48 (1966).

This research is supported by the Advanced Research Projects Agency and the Office of Naval Research

DIELECTRIC DISPERSION OF FERROELECTRICS

J. M. Ballantyne, Assistant Professor, Department of Electrical Engineering

M. Barnoski, J. Clark and B. Miao Research Assistants

Objective

To study lattice dynamics of ferroelectric crystals and their relationship to the phase transition and the ferroelectric state.

Approach

To measure reflection and transmission of electromagnetic energy at frequencies from microwaves to the visible using the techniques of far-infrared Fourier-transform interferometry, infrared spectroscopy and Raman spectroscopy.

Progress

The temperature dependence of the "soft" mode in KTaO_3 has been measured and reported. It was found that this mode is centered at 90 cm^{-1} and decreases in frequency as temperature decreases, but the breadth of the mode coupled with experimental inaccuracies prevents a meaningful quantitative comparison with Cochran's theory. Studies are progressing on the complete spectra of NaNO_2 and NaNO_3 . Arrangements have been made with groups in Chemistry and Astronomy for use of infrared spectrometers operating at shorter wavelengths than our interferometer, and these instruments are currently being used in the work on NaNO_2 and NaNO_3 .

A trial Raman spectrometer has been completed, and has yielded surprisingly excellent Raman spectra of BaTiO_3 single crystals. Lines separated by 15 cm^{-1} from the fundamental were resolved with a single monochromator.

A method for double-beam operation of our interferometer has been devised and reported. This system will greatly increase the precision of reflectance measurements on solids and is currently being installed.

PUBLICATIONS

"Far Infrared Dielectric Dispersion of Perovskites," J. M. Ballantyne, Proceedings of the International Meeting on Ferroelectricity, Prague, Vol. 1, 55 (1966).

"Double Beam Operation of a Fourier Spectrometer," J. M. Ballantyne, Applied Optics 6, 587 (1967).

This research is supported by the Advanced Research Projects Agency

HOLOGRAPHIC MICROSCOPE

J. M. Ballantyne, Assistant Professor, Department of Electrical Engineering

I. A. Abramowitz Research Assistant

Objective

To determine the theoretical limitations on the performance of a holographic microscope, develop a procedure for designing such instruments, and evaluate the theoretically optimum performance of several such designs.

Approach

Formulation and solution of theoretical equations for resolving power, depth of field, magnification, etc., of a holographic microscope and numerical solution of ray-trace equations subject to variable parameter constraints to minimize aberrations.

Progress

Theoretical work on the resolving power of a holographic microscope is nearing completion. Ray-trace equations have been numerically solved for cases of minimum aberration, and have yielded design relationships between such parameters as wavelength ratio, object and laser distances, hologram size, resolution, and magnification. Work is progressing on the design of specific "practical" systems.

PUBLICATIONS

"Evaluation of Hologram Aberrations by Ray Tracing," I. A. Abramowitz and J. M. Ballantyne, accepted by J.O.S.A. (1967).

This research is supported by the Advanced Research Projects Agency and the Cornell School of Electrical Engineering

MULTIPLE FREQUENCY MILLIMETER WAVE SOURCE

J. M. Ballantyne, Assistant Professor, Department of Electrical Engineering

J. Baukus, W. Wilson, A. Kohn and W. Frayer Research Assistants

Objective

To develop a broad band or multiple harmonic radiation source in the 5 to 0.5 millimeter region suitable for illuminating an interferometric spectrometer used in materials studies.

Approach

To study the harmonic and broad-band radiation from microwave oscillators made of III-V semiconductors, and of solid and gas-discharge harmonic generators, using a submillimeter interferometer and conventional microwave techniques.

Progress

A study of broad-band emission from InSb used in the "Larrabee" mode has been completed. Pulsed microwave emission at frequencies from 2-24 GHz was observed at peak powers on the order of milliwatts, and is reported in A. Kohn's Masters thesis. No emission above 24 GHz was observed, and thus the average power in this range must be below the 10^{-11} watt sensitivity of the bolometer used. "Low angle" emission peaks were observed for the first time with magnetic fields oriented $\pm 10-25^\circ$ and $\pm 155-170^\circ$ from the applied electric field. This mode of emission is explained as being a result of transverse breakdown which is a consequence of a large transverse Hall electric field.

Operational Gunn Effect diodes have been fabricated from epitaxial GaAs, and their high frequency and harmonic emission is currently under investigation.

Work is progressing on a new InSb device which is the solid-state analog of the magnetron, but will work at frequencies greater than 50 GHz. Samples are currently being fabricated.

PUBLICATIONS

"New Microwave Emission Effect in Indium Antimonide," A. Kohn, Proc. IEEE 55, 695 (1967).

This research is supported by the Advanced Research Projects Agency, the National Science Foundation and the Rome Air Development Center

RESEARCH ON A TUNNEL LASER

J. M. Ballantyne, Assistant Professor, Department of Electrical Engineering

R. Hunsperger and J. Rosenkrantz

Research Assistants

Objective

To perform a theoretical and experimental investigation of a new type of semiconductor laser in which the gain mechanism is substantially enhanced by confinement of the laser fields to the inverted population region where gain takes place.

Approach

To experimentally measure relevant parameters of photon loss using electron-beam pumping of homogeneous GaAs samples, and to observe luminescence from tunnel-injected carriers on MIS structures and determine optimum parameters for such structures on GaAs.

Progress

Photon loss has for the first time been measured in the active and passive regions of a GaAs laser. These measurements have been completed on a large number of both n- and p-type samples of different carrier concentrations. It was found that photon absorption is about ten times larger in passive GaAs than in active GaAs, although this difference depends strongly on doping density. Excellent agreement has been achieved with a theoretical model which allows two types of photon absorption mechanisms: transitions from valence to conduction bands (or close lying impurity levels) and transitions from lower to higher states in the conduction band. As a result of this work it is now possible to choose the optimum material for the tunnel laser.

A system for testing the tunnel laser has been completed, and has been used to make the first observation of luminescence from holes tunnel injected into n- type GaAs using an MIS structure.

PUBLICATIONS

"Measurement of Photon Absorption Loss in the Active and Passive Regions of a Semiconductor Laser," R. H. Hunsperger and J. M. Ballantyne, Appl. Phys. Letters 10, 130 (1967).

"A Study of Photon Loss in the Active and Passive Regions of a Semiconductor Laser," R. Hunsperger, Ph.D. Thesis, June 1967.

This research is supported by the Advanced Research Projects Agency and the U. S. Army Research Office - Durham

PROPERTIES OF INTERSTITIAL ATOMS IN FCC METALS PRODUCED BY ION BOMBARDMENT

R. W. Balluffi, Professor, Department of Materials Science and Engineering

L. E. Thomas Research Associate

D. Ast and T. Schober Research Assistants

Objective

To study the physical properties of interstitial atoms in fcc metals.

Approach

Interstitial atoms are produced by ion bombardment using metal ions of the same type as the target. Bombardment with low energy ions (~270 eV) produces interstitials via replacement collision sequences. Higher energy ions (~50 KeV) produce interstitials via channeling. Interstitial defects are observed by transmission electron microscopy.

Progress

The formation of point defect clusters in gold foils due to 270 eV gold ion bombardment at temperatures from -90°C to +100°C was investigated. Radiation-induced defect clusters were observed under certain conditions which consisted solely of interstitial type dislocations lying within about 100 Å of the surface. It was concluded that this damage was formed by the aggregation of interstitial point defects produced by replacement collision sequences. No damage was found in clean gold foils bombarded with gold ions above -30°C. However, below -30°C increasing damage formed with decreasing temperature. Further auxiliary experiments revealed that carbonaceous surface layers produced by the interaction of electron or ion beams with hydrocarbon molecules at the specimen surfaces before or during ion bombardment caused a considerable density of observable damage at all temperatures. Similar damage enhancement was found in clean specimens bombarded with argon ions instead of gold ions. It was concluded that all of the interstitial damage was nucleated by hydrocarbon or argon impurities which were driven short distances into the specimens. The damage found in the ostensibly clean specimens at temperatures below -30°C was attributed to unavoidable hydrocarbon contamination caused by trapping at the cold specimen surfaces.

Experiments involving the annihilation of vacancy precipitates in thin specimens by mobile interstitials were also carried out, and it was shown that all the results were consistent with an interstitial which is already mobile at -90°C.

R. W. Balluffi

A new gold ion accelerator capable of producing 50 KeV gold ions has been constructed and is in successful operation. Experiments in which gold ions are channeled along $\langle 110 \rangle$ directions to produce interstitials in gold single crystals are in progress.

A further low energy (100-300 eV) acceleration unit which will operate under ultra high vacuum conditions for ion bombarding specimens possessing atomically clean surfaces has been partially constructed.

PUBLICATIONS

"Low Energy Bombardment of Gold with Gold Ions: On Interstitial Atom Migration in Stage III," L. E. Thomas and R. W. Balluffi, Appl. Phys. Letters 9, 171 (1966).

"Interstitial Defect Clusters in Gold After Bombardment with 270 eV Gold Ions," L. E. Thomas and R. W. Balluffi, accepted for publication, Phil. Mag. 1967.

"Mobility of Interstitial Defects in Gold Bombarded with 270 eV Gold Ions in Stage III," L. E. Thomas and R. W. Balluffi, accepted for publication, Phil. Mag. 1967.

"Low Energy Gold Ion Bombardment of Gold," L. E. Thomas, Ph.D. Thesis, Cornell University, September 1966.

This research is supported by the Atomic Energy Commission

ANNEALING OF VACANCY DEFECTS IN QUENCHED METALS

R. W. Balluffi and D. N. Seidman, Professor and Assistant Professor,
Department of Materials Science and Engineering

R. W. Siegel and L. E. Thomas Research Associates

C. G. Wang, R. J. Sonoff and A. DasGupta Research Assistants

Objective

A study of the annealing of quenched-in vacancy defects in metals. Interest is centered on the physical properties of the defects themselves and on the way in which they precipitate or else are absorbed at sinks such as, for example, dislocations.

Approach

Thin wire (or ribbon) shaped specimens are rapidly quenched and then annealed. The annealing of the supersaturated vacancy defects is studied by measuring the electrical resistivity of the defects. The specimen defect structure is also investigated by transmission electron microscopy.

Progress

A study of the resistivity annealing of vacancies in quenched platinum was started. The specimen microstructures were observed by transmission electron microscopy. Measurements of the residual resistivity at 4.2°K showed that platinum may be purified by long time heating in air near the melting point in the same way as gold. A technique for electropolishing specimens for transmission microscopy at -35°C was developed which allowed, for the first time, the observation of the structure of quenched and annealed platinum.

The efficiency with which vacancy stacking fault tetrahedra absorb supersaturated vacancies in gold was studied by observing the competition between tetrahedra and free surfaces for migrating vacancies during the annealing of quenched gold.

A new technique was developed for studying the annealing of supersaturated vacancy defects at elevated temperatures in gold. A wire specimen, mounted in a He-filled cryostat immersed in liquid nitrogen, was quenched and annealed as follows: (i) the resistance heated specimen was gas quenched from 700°C to an annealing temperature (200-670°C) where it was held steady for periods between 100 msec and 10 min; (ii) the specimen was finally gas quenched to 78°K. The loss of supersaturated vacancies to dislocations during (i) and (ii) was obtained from electrical resistivity measurements at 4.2°K. The temperature-time history was obtained with a precision rapid data acquisition system which (1) recorded, in analog form, the potential drops in the resistivity measuring circuit; (2) converted the analog

R. W. Balluffi and D. N. Seidman

Progress - continued

data into digital form and stored them in a magnetic memory unit (the maximum speed was 4000 readings sec^{-1}); (3) punched the stored data onto tape which was fed into a computer for conversion to temperature-time data. The results were found to fit a temperature dependent diffusion controlled monovacancy-divacancy annealing model to dislocations possessing a relatively high divacancy binding energy in agreement with our earlier work.

PUBLICATIONS

"Electropolishing of Platinum Foils at -35°C for Transmission Electron Microscopy," C.T.J. Ahlers and R. W. Balluffi, J. Appl. Phys. 38, 910 (1967).

"Annealing Kinetics of Vacancy Defects in Quenched Gold at Elevated Temperatures," C. G. Wang, Ph.D. Thesis, Cornell University, June 1967.

This research is supported by the Atomic Energy Commission

DIFFUSION ALONG DISLOCATIONS

R. W. Balluffi, Professor, Department of Materials Science and Engineering

H. G. Bowden Research Associate

T. Volin Research Assistant

Objective

To study rates of diffusion along dislocations in metals

Approach

Spherical voids are produced in thin metal foils. These are connected to the free surfaces by dislocations, and the rate at which atoms are transported along the dislocations into the voids is studied using transmission electron microscopy. Dislocation dipoles are produced, and the rate at which they circularize by mass transport along the dipoles is studied.

Progress

By controlling the quenching conditions the excess vacancies produced in quenched aluminum were precipitated as spherical voids in sheet specimens. Specimens containing these voids were then electrothinned for transmission electron microscopy. By critically straining these specimens dislocations were produced which in many cases hooked up the voids to the specimen surface. Upon subsequent annealing the tendency of the dislocation diffusion pipes to preferentially transfer atoms into the voids from the surface was investigated. Preliminary results indicate that the voids which were connected to the surface by dislocations often annealed out faster than the isolated voids. Quantitative data describing this effect are being gathered.

Dislocation dipoles have been obtained in aluminum, copper and gold, by subjecting them to low temperature fatigue. These dipoles have then been annealed and observed by means of hot stage electron microscopy. During annealing the dipoles shrink extensively by decreasing either their length or width. In no case has any "breaking up" or circularization of the dipoles (as seen, for example, in zinc by Price) been observed as the result of conservative pipe diffusion processes. These studies are being continued.

This research is supported by the Atomic Energy Commission

DYNAMICAL DIFFRACTION OF X-RAYS

B. W. Batterman, Associate Professor, Department of Materials Science
and Engineering

G Hildebrandt

Research Associate

Objective

- a. By measuring the beating of x-ray wave fields of Ge to determine the atomic scattering factor.
- b. To try to establish the existence of the beating phenomenon (Pendellösung) in the reflection case.

Approach

- a. Wedges and flat-faced crystals of Ge are investigated with x-rays and the beat period and intensity are observed.
- b. Thin crystals of Si ($\approx 10\mu$) are used to diffract a highly monochromatic x-ray beam.

Progress

- a. Two independent measurements have been made of the atomic scattering factor by the Pendellösung method which were found to be in excellent agreement with each other, but different from the values obtained with the flat faced reflection technique. The differences are outside experimental error and may indicate that the theory may not describe both phenomena adequately.
- b. It is believed that for the first time Pendellösung phenomena in the reflection case have been observed.

This research is supported by the Advanced Research Projects Agency

LOW TEMPERATURE DIFFRACTION IN TYPE II SUPERCONDUCTORS (PART II:
 Nb_3Sn)

B. W. Batterman, Associate Professor, Department of Materials Science
and Engineering

R. Mailfert Research Assistant

Objective

To look for cubic tetragonal transformation at low temperature
in Nb_3Sn .

Approach

X-ray and optical techniques are used to look for a structural
transformation upon cooling.

Progress

Initially single crystals of Nb_3Sn did not show any signs of
a phase transformation on being cooled at 5°K. However, after heat
treating to remove dissolved gases and a small amount of Sn, the
transformation could be observed. The cell size has been established
as a function of temperature as well as the transition temperature
and the arrest of the transformation when the sample goes super-
conducting at 18°K.

PUBLICATIONS

"Low Temperature Structural Transformation in Nb_3Sn ," R. Mailfert,
B. W. Batterman and J. J. Hanak, Physics Letters, March 1967.

This research is supported by the Advanced Research Projects Agency

PHONON DISPERSION IN VANADIUM

B. W. Batterman, Associate Professor, Department of Materials Science
and Engineering

B.M.S. Kashyap Research Associate

Objective

To measure the phonon dispersion in Vanadium. This is to complete the V, Ta, Nb series. Neutron diffraction experiments have determined the dispersion in Ta and Nb but the technique is not applicable to V because of its very low neutron coherent scattering cross section.

Approach

Measurements are made of the diffuse scattering of x-rays from single crystals of Vanadium. This is corrected for Compton and air scattering, and the resultant thermal scattering is converted to the frequency of the phonon.

Progress

Complete phonon dispersion curves have been measured for both polarizations in the three principle crystallographic directions. The curves are qualitatively similar to Nb and Ta but show much larger dispersion at low frequencies than Nb and Ta. Discontinuities in the dispersion have been observed, but the lack of experimental information on the Fermi surface of V precludes speculation that these may be Kohn anomalies.

This research is supported by the Advanced Research Projects Agency

ANHARMONIC VIBRATIONS IN CaF_2

B. W. Batterman, Associate Professor, Department of Materials Science
and Engineering

H. Strock Research Assistant

Objective

To establish that the fluorine atom vibrates anharmonically as indicated by neutron diffraction measurements.

Approach

The integrated reflection intensities from single crystals of CaF_2 are measured as a function of temperature. From the temperature variation from different diffracting planes it can be determined whether the vibrational amplitude is harmonic or not.

Progress

Measurements of two reflections as a function of temperature have given results in reasonable agreement with neutron diffraction.

This research is supported by the Advanced Research Projects Agency

LOW TEMPERATURE DIFFRACTION IN TYPE II SUPERCONDUCTORS (PART I: V_3Si)

B. W. Batterman, Associate Professor, Department of Materials Science
and Engineering

J. Perel Research Associate

R. Mailfert and J. Wanagel Research Assistants

Objective

To study the properties of the low temperature phase transformation in V_3Si .

Approach

(1) V_3Si - Search for sub-lattice distortion predicted from thermodynamic and symmetry arguments by looking for the appearance of diffraction lines forbidden in the cubic phase.

(2) Explain the possibility of observing the transformation optically by low temperature light microscopy.

Progress

(1) An upper limit to the possible sub-lattice distortion for the various possible allowed distortions has been established.

(2) It was possible to show that the low temperature phase transformation can be seen optically, not only for V_3Si , but for the newly discovered transformation in Nb_3Sn (see part II).

This research was supported by the Advanced Research Projects Agency
and the Atomic Energy Commission

ELECTRON DIFFRACTION INVESTIGATIONS

S. H. Bauer, Professor, Department of Chemistry

L. Hencher Research Associate

R. Hildebrandt Research Assistant

Objective

To complete the development of a parallel incidence electron diffraction apparatus; to exploit its special features for determination of the atom form factors for electron scattering at small angles; to determine structures of molecular species in vapor phase for materials which have relatively low vapor pressures.

Approach

The determination of atom form factors hinges on the ability to construct a rotating sector of known aperture which is free from undulations and to calibrate it. It is possible to calibrate the sector by measuring differential scattering from a homologous set of compounds. The parallel incidence mode is specifically suited for work with low vapor pressure materials. Three high temperature sample holders and nozzles have been constructed to cover the temperature range 350°-2000°K. These will be used as needed for study of vapors such as LiAlF_4 , BaF_2 , etc.

Progress

Diffraction patterns of about a dozen compounds which have adequate volatility at room temperature have been obtained with the apparatus operating in the convergent beam mode. Their structures are being analyzed at the present time. The atom form factor for carbon is being determined using the parallel incidence mode. In addition, one of the principal objectives of this exercise was to set up the routine for structure analyses as part of the program. This involves (a) operation of the apparatus, (b) techniques for data reduction (plate handling, microdensitometry, etc.), (c) sector design, computational programs, etc. This phase is essentially completed except for the problem of sector construction and calibration. A new procedure is being tested for obtaining carefully machined sectors and various tests are being made for reducing the background scattered radiation and further to enhance control of plate handling and microdensitometry.

PUBLICATIONS

"The Dynamics of Cryosorption Pumping," S. H. Bauer and F. Jeffers, J. Phys. Chem. 69, 3317 (1965).

S. H. Bauer

PUBLICATIONS - continued

"The Structures of C_6 , B_3N_3 and C_3N_3 Ring Compounds," S. H. Bauer, K. Katada and K. Kimura, L. Pauling's 65th Anniversary Festschrift (in press).

"An Electron Diffraction Study of the Structures of NF_2 and N_2F_4 ," R. K. Bohn and S. H. Bauer, Inorg. Chem. 6, 304 (1967).

"An Electron Diffraction Study of the Structures of cis- and trans- N_2F_2 ," R. K. Bohn and S. H. Bauer, Inorg. Chem. 6, 309 (1967).

"The Molecular Structure of Perfluorodiazirine," J. Am. Chem. Soc. (in press).

This research is supported by the Advanced Research Projects Agency, the National Science Foundation and the Office of Naval Research

KINETICS OF SOLID-LIQUID PHASE TRANSITIONS

J. M. Blakely, Associate Professor Department of Materials Science
and Engineering

D. Olson Research Assistant

Objective

To study the atomic mechanisms of solidification in high purity metals and the relationship between interface velocity and under-cooling.

Approach

To measure the motion of a solid-liquid interface in response to a low frequency thermal wave.

Progress

In high purity tin, experiments indicate that the velocity - under-cooling relationship is linear. Experiments now being completed are designed to investigate the frequency response of the system.

PUBLICATIONS

"Kinetics of the Solid-Liquid Transition in Tin", D. A. Rigney and J. M. Blakely, *Acta Met.*, 14, 1371, (1966).

"Comment on Kinetics of Solid-Liquid Transition in Tin", D. A. Rigney and J. M. Blakely, *Acta Met.* (letter), 14, 1384, (1966).

"Sinusoidal Temperature Wave Generating System", D. A. Rigney, *Rev. Sci. Instr.*, 37, 1376, (1966).

This research is sponsored by the Advanced Research Projects Agency

DEFECTS AND DIFFUSION AT IONIC CRYSTAL SURFACES

J. M. Blakely, Associate Professor, Department of Materials Science
and Engineering

J. M. Baker and R. Poeppel Research Assistants

Objective

To study the distribution of point defects at and near free surfaces of ionic crystals.

Approach

Measurement of variation of surface potential with temperature in vacuum by the vibrating capacitor method; surface excess conductance measurements; mass transport diffusion.

Progress

Experiments are now in progress on variations of surface potential of KCl and AgCl single crystals with temperature and the magnitude of excess surface conductance.

PUBLICATIONS

"Grain Boundary Grooving at a Solid-Solid Interface," A. H. Feingold, J. M. Blakely, and C. Y. Li, Proceedings of Int. Symposium on Special Topics in Ceramics, Alfred. New York (1967).

"An Experimental Technique to Study Composite Interfaces"
A. H. Feingold, J. M. Blakely and C. Y. Li, M.S.C.
Report 536 (1966).

This research is supported by the Advanced Research Projects
Agency and the Air Force Office of Scientific Research

SURFACE STRUCTURE, DIFFUSION AND SURFACE ENERGIES

J. M. Blakely, Associate Professor, Department of Materials Science
and Engineering

R. Pichulo and J. C. Tracey Research Assistants

Objective

To investigate (i) the mechanisms of atom movements on metal single crystal surfaces and (ii) the absolute and relative surface energies as a function of crystallographic orientation, temperature and purity.

Approach

Measurement by interference microscopy and optical diffraction methods of the relaxation rates of sinusoidal single crystal surfaces at high temperatures under ultra high vacuum conditions.

Progress

A set of experiments on single crystals of nickel have been completed. These experiments show that the activation energy for surface diffusion is ~ 1.5 to 1.85eV depending on orientation and direction. From studies on (111), (100), and (110) surfaces surface diffusivities are found to vary by a factor of < 2 with direction or orientation. Facilities for inert gas ion bombardment, controlled gas leak and gas analysis have been set up. A set of experiments on W single crystal surfaces are now in progress. A number of other studies have been made on W surfaces including measurements of adsorbed ion mobilities. Mass transport experiments of the type being performed here are required to establish defect energies and concentrations.

PUBLICATIONS

"Surface Self-Diffusion and Surface Energy of Nickel," P. S. Maiya and J. M. Blakely, J. Appl. Phys. 38, 698, 1967.

"Surface Energies from Transport Studies," P. S. Maiya and J. M. Blakely, Proceedings of Sagamore Conference "Characteristics of Interfaces".

"A Study of Surface Self-Diffusion and Surface Energy in Nickel," P. S. Maiya, Ph.D. Thesis, September 1966.

This research is supported by the Advanced Research Projects Agency

MAGNETIC PHENOMENA IN SUPERCONDUCTORS

R. Bowers, Professor, Department of Physics

B. W. Maxfield Acting Assistant Professor

C. G. Stephan Research Assistant

Objective

To study low frequency electromagnetic resonances that were observed in superconductors.

Approach

The project has required a development of techniques for quantitative measurements of low frequency signals that are much smaller than the noise level. These include techniques in electronic instrumentation and cryostat construction.

Progress

Low frequency resonances have been observed in the intermediate state of pure indium and the mixed state of pure niobium. The general character of these resonances is the same as that of helicon propagation in a normal metal, i.e., the dispersion relation is qualitatively the same. However the dependence of the resonance parameters upon external variables is much different from the normal helicon. The temperature dependence of the resonance parameters is primarily determined by the temperature dependence of the critical field. As yet, the mechanism giving rise to these resonances is not well understood but the Hall effect in the normal regions of the intermediate and mixed states seems to play an important role.

PUBLICATIONS

"Audio Frequency Electromagnetic Properties of Normal and Superconducting Indium." E. F. Johnson, Ph.D. Thesis, June 1967.

"Observations of Low-Frequency Mixed State Resonances in Pure Niobium." B. W. Maxfield and E. F. Johnson, Phys. Rev. Lett. 16, 652 (1966).

"Damping of Helicon Resonances in Pure Type II Superconductors," B. W. Maxfield, Solid State Communications 5 (1967).

"Helicon Resonances in Niobium near H_{c2} ", B. W. Maxfield, Phys. Rev. Lett. 19 (1967).

This research is supported by the Atomic Energy Commission

MAGNETIC PHENOMENA AND ELECTRONIC STRUCTURE

R. Bowers, Professor, Department of Physics

B. W. Maxfield Acting Assistant Professor

J. R. Merrill Research Associate

J. C. Garland and J. R. Houck Research Assistants

Objective

To study the propagation characteristics of plasma waves (helicon waves) in metals and to use these waves to probe the electronic structure of metals.

Approach

Instrumentation techniques have been developed for the detection and quantitative study of helicon waves over a wide range of frequencies. Also single crystals of metals have been grown and prepared for use in the determination of electronic structure by using helicon waves.

Progress

Quantitative measurements have been made of the collisionless damping of propagating helicon waves in the simple metals, Na and K. Agreement was found with the free electron theory prediction to within a few percent. Magnetoresistance measurements on single and polycrystalline K show the previously observed linear magnetoresistance, but in this experiment no probes were attached to the specimen. This is an important result because the previous linear magnetoresistance was attributed to spurious probe effects and presents clear evidence that the observed linear increase is related to crystalline strain. The anisotropy of the magnetoresistance and the Hall effect in single crystals of Al, Ag and Cu has been determined for a number of crystalline symmetry directions by measuring the resonance parameters of a helicon standing wave. These results agree well with conventional measurements and show that the helicon may be a useful tool in determining the anisotropy of certain electronic parameters. The helicon technique is especially useful if a probeless method is essential.

PUBLICATIONS

"Aspects of Helicon Propagation in Metals," J. R. Merrill, Ph.D. Thesis, September 1966.

"The Magnetoresistivity of Potassium as Measured by Helicon Waves," P. A. Penz, Ph.D. Thesis, June 1967.

"A Solid State Source of Microwaves," R. Bowers, Scientific American 215, 2, 22-31 (1966).

R. Bowers

PUBLICATIONS - continued

"Direct Electromagnetic Generation of Acoustic Waves," J. R. Houck,
H. V. Bohm, B. W. Maxfield and J. W. Wilkins, Phys. Rev. Lett.
19, 224 (1967).

"The Propagation of Helicon Waves under Conditions of Nonlocal Conductivity," J. R. Houck, Ph.D. Thesis, June 1967.

This research is supported by the Atomic Energy Commission

ADHERENCE AND WETTABILITY OF METALS TO SAPPHIRE

M. S. Burton, Professor, Department of Materials Science and Engineering

Objective

To study the effect of atmosphere and alloy additions on the surface tension and contact angle of nickel on sapphire.

Approach

Sessile drops of metallic alloys were solidified on sapphire substrates. Contact angles, and the stress to shear the drops from the substrate were measured, and the interface structure determined by microscopy and electron microprobe analysis.

Progress

The work on titanium and chromium additions to nickel alloys was completed early in the year. Results of the work were published during the year.

The liquid-gas surface tension of nickel on sapphire is 1750 ergs per sq. cm. with a contact angle of 110 deg. The results are not affected appreciably by vacuum, argon, or hydrogen atmospheres. Small additions of chromium or titanium decrease the contact angle. Adhesion in the nickel-alumina system is by formation of $\text{NiO} : \text{Al}_2\text{O}_3$ spinel; in the titanium alloy-alumina system by mechanical interlocking; and in the chromium alloy-alumina system by a solid solution involving Cr_2O_3 and Al_2O_3 .

PUBLICATIONS

"Adherence and Wettability of Nickel, Nickel-Titanium Alloys, and Nickel-Chromium Alloys to Sapphire." J. E. Ritter and M. S. Burton, Trans. AIME 239 (1967).

This research is supported by the Advanced Research Projects Agency

PHONON PHYSICS (THEORETICAL)

P. Carruthers, Associate Professor, Department of Physics

K. S. Dy Research Associate

D. Hyman Research Assistant

Objective

(1) Study of irreversible processes in systems of phonons interacting with each other and with defects in (a) solids and (b) liquid helium.

(2) Clarification of meaning of phase variables in quantum mechanics, especially Bose systems.

Approach

(1) A new method of analyzing the density matrix equation of motion has been developed. The method employs the so-called coherent states.

(2) A rigorous approach to quantum mechanical phase variables has been undertaken.

Progress

(1) The Peierls master equation was established by K. S. Dy. In his thesis the corresponding transport equation (including temperature gradients) was successfully derived.

(2) Mr. D. Hyman has been studying sound attenuation in $\text{He}^3\text{-He}^4$ mixtures. He is also studying the applicability of coherent state concepts to superfluid states.

(3) K. S. Dy (working with Wu) has finished a study of the cohesive energy of metallic hydrogen. Coherent states have been shown to provide a powerful method of analyzing this problem.

PUBLICATIONS

"Coherent States and Irreversible Processes in Anharmonic Crystals,"
P. Carruthers and K. S. Dy, Phys. Rev. 147, 214 (1966).

"Phase and Angle Variables in Quantum Mechanics," P. Carruthers and
M. M. Vieto, Rev. Mod. Phys. (in press).

"Coherent State and its Application to Quantum Statistical Mechanics,"
K. S. Dy, Ph.D. Thesis, June 1967.

This research is supported by the Atomic Energy Commission and the
Office of Naval Research

THE ENERGY OF A QUANTIZED VORTEX LINE IN SUPERFLUID HELIUM

G. V. Chester, Professor, Department of Physics

R. Metz Research Assistant

Objective

To calculate the energy of a vortex line and vortex ring in liquid helium four. The energy of the latter can be compared with the experimental values of Reif and Rayfield.

Approach

Two different trial wave functions have been constructed, all of which are orthogonal to the ground state. These will be used in variational calculations to obtain the lowest energy state for a given circulation.

Progress

The machine computations that are necessary for the first of these trial wave functions have been programmed and the first energies have been obtained. Preliminary indications are that they will be in good agreement with those of Reif and Rayfield.

This research is supported by the Advanced Research Projects Agency

THE EIGENVALUE SPECTRUM OF THE PHONON BOLTZMAN EQUATION

G. V. Chester, Professor, Department of Physics

E. Tobenfeld Research Assistant

Objective

To find the eigenvalue structure of the phonon Boltzman equation and in particular to see whether the current derivations of "phonon hydrodynamics" can be justified.

Approach

The same approach used by MacLennan and Grad in the corresponding classical problem for a dilute gas will be followed.

Progress

The mathematical difficulties in the problem have been isolated and it is now clear that some generalizations of Grad's work will be required before "phonon hydrodynamics" can be justified.

This research is supported by the Advanced Research Projects Agency and the
National Science Foundation

THE EXCITATION SPECTRUM OF HELIUM FOUR

G. V. Chester, Professor, Department of Physics

A. Widom, Research Assistant

Objective

To calculate and interpret the excitation spectrum of liquid helium four and the effective mass of helium three impurities in helium four.

Approach

A new variational method has been devised by Mr. Widom which is sufficiently simple that it will be possible to compute this spectrum for all values of the momentum of the excitations. This variational principle can also be applied to the effective mass problem.

Progress

Preliminary calculation shows that the energy of the roton minimum is very close to that obtained by Feynman and Cohen.

PUBLICATIONS

"The Motion of Impurities and the Spectrum of Excitations in Liquid Helium Four," T. Burke, G. V. Chester, and K. Major, *Annals of Physics* 42, 144 (1967).

This research is supported by the Advanced Research Projects Agency and the National Science Foundation

PHONONS AND THE PROPERTIES OF A BOSE SYSTEM

G. V. Chester, Professor, Department of Physics

L. Reatto Research Associate

Objective

To construct a wave function and density matrix which correctly reflects the ability of a Bose system to propagate long wavelength phonons, and to examine the influence of these phonons on the physical properties of the system.

Approach

It is assumed that for small enough wave numbers k , the density variables ρ_k perform harmonic oscillations independently of any other modes of motion. This assumption leads to an approximate wave function and density matrix.

Progress

The numerical work has been reported under the project - "The Ground State of Liquid Helium Four." Dr. Reatto has completed an analysis of the influence of the phonon modes on the appearance of Bose-Einstein condensation and has found that they inhibit this kind of condensation at any temperature in one dimension and prevent its occurring at any finite temperature in two dimensions.

PUBLICATIONS

"Phonons and the Properties of a Bose System," L. Reatto and G. V. Chester, Phys. Rev. 155, 88 (1967).

This research is supported by the Advanced Research Projects Agency and the Atomic Energy Commission

THE GROUND STATE OF LIQUID HELIUM FOUR

G. V. Chester, Professor, Department of Physics

L. Reatto Research Associate

W. Francis Research Assistant

Objective

To calculate the ground state properties; the energy, the structure factor $S(k)$, the equation of state and the fraction of particles in the zero momentum state, using the new variational wave function proposed by this group in recent studies.

Approach

The binding energy will be calculated variationally using approximate integral equations for the pair distribution function. When the best ground state has been found in this way the other properties can be calculated directly.

Progress

The best ground state and the accompanying structure factor have been found using the Percus-Yevick integral equation, and little change has been found in the energy from the infinite range correlations introduced by the zero point motion of the phonons. The structure factor $S(k)$ is much improved at small momentum transfers as compared with previous calculations by Macmillan and Verlet. The equation of state is rather poor, however.

PUBLICATIONS

"The Ground State of Liquid Helium Four," G. V. Chester and L. Reatto, Physics Letters 22, August 1966.

This research is supported by the Advanced Research Projects Agency, the Union Carbide Corporation and the Atomic Energy Commission

THE DERIVATION OF BOLTZMANN EQUATIONS FROM MASTER EQUATIONS

G. V. Chester, Professor, Department of Physics

J. Sykes Research Associate

Objective

To derive the conventional Boltzmann equations from the appropriate master equations.

Approach

A generalization of Kac's factorization theorem has been obtained and this immediately leads to the required derivations.

Progress

The Boltzmann equation for any mixture of Bosons and Fermions has been derived and in particular that conventionally used in metal physics to describe the interactions of electrons and phonons has been rigorously derived.

PUBLICATIONS

"Factorization Theorems", G. V. Chester and J. Sykes, Journal of Mathematical Physics 1, 2243 (1966).

"The Relationship Between Linear Response Theory and the Boltzmann Equation for a Weakly Interacting System of Electrons and Phonons", G. V. Chester and J. Sykes, Journal of Math. Phys. 1, 2251 (1966).

This research is supported by the Advanced Research Projects Agency and the National Science Foundation

ANALYSIS OF STRESSES AND DISPLACEMENTS INDUCED IN MULTIFIBER COMPOSITES

H. D. Conway, Professor, Department of Theoretical and Applied Mechanics

C. S. Chang

Research Assistant

Objective

To compute the bond stresses, displacements and effective moduli of multifiber composites.

Approach

Approaches used up to the present have been numerical for one-dimensional fibers distributed in rows and columns and exact, complex-function, techniques for two-dimensional rectangular fibers. These techniques will be combined in specific problems as required.

Progress

The normal and shearing stresses have been computed on the boundaries of rigid rectangular fibers which are sufficiently far apart in the matrix so as not to interfere with one another. These exact solutions were compared with the results of photoelastic tests by Dr. D. M. Schuster, Department of Materials Science and Engineering, and showed good agreement.

Numerical data have also been obtained for rows and columns of one-dimensional fibers by a numerical technique yielding results comparable with the above exact ones. The effect of non-rigid fibers is presently being investigated and preliminary results are satisfactory. Means for reducing stress concentrations are being considered.

This research is supported by the Advanced Research Projects Agency

MEASUREMENT OF COEFFICIENT OF SELF-DIFFUSION IN LIQUID LITHIUM

R. M. Cotts, Associate Professor, Department of Physics

J. Murday Research Assistant

Objective

To measure the coefficient of self-diffusion of lithium in the liquid state at temperatures near the melting point.

Approach

To use the spin-echo technique, with large pulsed magnetic field gradients, to measure D (coefficient of self-diffusion). The echo signal amplitude is measured as a function of gradient pulse amplitude and width. D is measured at several temperatures between 185°C and 250°C.

Progress

D has been determined to an accuracy of +10%. Calibrations and internal consistency checks are now being made. It has been found that

$$D = 6.2 \pm 0.7 \times 10^{-5} \text{ cm}^2/\text{sec at the melting point and that} \\ (\Delta D/\Delta T) = +0.033 \pm 0.01 \times 10^{-5} \text{ cm}^2/\text{sec between 185°C and 250°C.}$$

PUBLICATIONS

"Nuclear Magnetic Resonance Study of Self-Diffusion in a Bounded Medium,"
R. C. Wayne and R. M. Cotts, Phys. Rev. 151, 254 (1966).

This research is supported by the Advanced Research Projects Agency and
the National Science Foundation

NUCLEAR MAGNETIC RESONANCE AND ELECTRONIC SPECIFIC HEAT OF VANADIUM - CHROMIUM HYDRIDES

R. M. Cotts, Associate Professor, Department of Physics

D. Rohy Research Assistant

Objective

To prepare hydrides from V-Cr alloys. To study effects of hydriding upon the conduction band of the host metal by measurements of Knight Shifts, spin-lattice relaxation times of the V resonance, and the electronic specific heat. Comparisons are made between V-H, V-Cr, and V-Cr-H systems. Diffusion kinetics of hydrogen ions will also be studied.

Approach

Vanadium Knight Shift measurements are made with a C.W. spectrometer as a function of temperature. Spin-lattice relaxation times are measured as a function of temperature by pulsed techniques. Similar measurements are made on protons to determine diffusion activation energies. Specific heats of V, V-Cr, and V-Cr-H will be measured and the changes in electronic specific heat will be determined as functions of Cr and H concentrations.

Progress

Knight shifts (K) of V have been measured in $V_{(1-x)}Cr_xH_y$ for values of x ranging from 0-0.4 and y ranging from 0-0.75. Spin lattice relaxation times (T_1) of V and H have been measured in the alloys. Results indicate that the K and T_1 data depend only upon an electron/atom ratio (e/a) where (e/a) is the number of conduction electrons per transition metal ion. The value of (e/a) is determined from $5(1-x) + 6x + y$. These results are interpreted to mean that the hydrogen exists as a positive ion which has lost its electron to the conduction band of the metal.

The electronic specific heat apparatus has been constructed and measurements are in progress.

This research is supported by the Advanced Research Projects Agency and the National Science Foundation

NMR AT LOW TEMPERATURES

R. M. Cotts, Associate Professor, Department of Physics

D. Miyoshi Research Assistant

Objective

To study the effect of alloying on the nuclear-conduction electron hyperfine interaction of the solute atom.

Approach

To measure spin-lattice relaxation times of solutes in various host lattices at low temperatures.

Progress

Measurement of T_1 of Tl in the Tl-Pb system has been made in 10% Tl alloy. An amplifier for use immersed in liquid helium has been developed.

This research is supported by the Advanced Research Projects Agency and the National Science Foundation

NMR STUDY OF Li IN KCl

R. M. Cotts, Associate Professor, Department of Physics

D. Alderman Research Assistant

Objective

To study the symmetries of the states of Li in KCl by observation of nuclear electric quadrupole interaction produced by electric and strain fields.

Approach

The Li^7 NMR is observed in KCl crystals, which contain 3×10^{18} Li^+ ions per cm^3 , by the CW technique using a bridge type spectrometer. It is planned to induce an electric quadrupole interaction with the Li^7 nucleus by suitable application of a large D.C. electric field or an axial stress in the crystal. The symmetry and size of the quadrupole interaction will be studied.

Progress

Cryostats for application of electric and strain fields have been constructed. Observations of NMR of Li^7 have been made at 1.3°K with adequate s/n ratio. Quadrupolar effects due to strain have been observed, while the electric field experiment has produced a null effect.

This research is supported by the Advanced Research Projects Agency and the National Science Foundation

CRITICAL CORRELATIONS AND INTERACTIONS WITH LATTICE MODES

M. E. Fisher, Professor, Department of Chemistry

R. E. Hartwig Research Associate

Objective

To study theoretically the behavior of correlation functions near critical points and to determine the changes in the nature of the critical point, if any, caused by interactions with other degrees of freedom, particularly lattice vibrations.

Approach

By exact mathematical analysis of various model systems exhibiting critical points especially the plane Ising model ferromagnet and a one-dimensional many-body interaction model (related to the droplet picture of condensation).

Progress

Apart from some initial studies of the many-body interaction model attention has been mainly directed to the analysis of the Toeplitz determinants representing the spin-spin correlation functions of the plane Ising model. New exact results for the triangular and honeycomb lattices have been obtained. Rigorous justification has been given for the various steps in T. T. Wu's recent work on the problem and his implicit iterative method has been proved convergent. This approach has been reformulated in a simpler fashion and applied to a related class of Toeplitz matrices.

PUBLICATIONS

"Toeplitz Determinants and Szegő's Formula", R. E. Hartwig,
Australian J. Math (1967).

This research is sponsored by the Advanced Research Projects Agency
and the National Science Foundation

STATISTICAL MECHANICS OF HYDROGEN-BONDED FERROELECTRICS AND RELATED SYSTEMS

M. E. Fisher, Professor, Department of Chemistry

J. F. Nagle Research Associate

Objective

To understand the behavior of hydrogen-bonded ferroelectrics and related physical systems particularly near their critical and transition points. To develop the appropriate statistical mechanical techniques, notably graph-combinatorial series expansions.

Approach

To analyze available data on critical behavior; and to study lattice models of hydrogen-bonded systems using the method of exact series expansions combined with the ratio and Padé approximate techniques; to evaluate and extrapolate the series obtained.

Progress

The work has continued previous work on the cooperative properties of hydrogen bonds in ice and certain models of ferroelectrics and antiferroelectrics. A better understanding of the thermal properties of KDP (KH_2PO_4) and its homeomorphs has been achieved and experimental data have been reanalyzed to determine critical exponents. The theory of the F-model of an antiferroelectric has also been extended.

The task of obtaining longer exact series expansions for reliable and accurate analysis leads to various graph combinatoric problems. A new, very general technique has been developed for handling these problems. It simplifies and allows the extension of series calculations for a variety of models already studied by other techniques, but also promises results on various new models exhibiting phase transitions.

PUBLICATIONS

- "Lattice Statistics of Hydrogen Bonded Crystals I. The Residual Entropy of Ice," J. F. Nagle, J. Math. Phys. 7, 1484 (1966).
" " - " II. The Slater KDP Model and the Rys F. Model," J. F. Nagle, J. Math. Phys. 7, 1492 (1966).
"On Ordering and Identifying Undirected Linear Graphs," J. F. Nagle, J. Math. Phys. 7, 1588 (1966).
"New Series Expansion Method for the Dimer Problem," J. F. Nagle, Phys. Rev. 152, 190 (1966).

M. E. Fisher

PUBLICATIONS - continued

"A New Method for Combinatorial Problems on Graphs", J. F. Nagle,
Proc. Int. Seminar on Graph Theory, Rome (1966), in press.

This work is supported by the Advanced Research Projects Agency

STATISTICAL MECHANICS OF FINITE SYSTEMS

M. E. Fisher, Professor, Department of Chemistry

A. E. Ferdinand Research Assistant

Objective

To study the contributions to the free energy of finite systems associated with the boundary and with interfaces between different phases, especially in the region of critical points.

Approach

In the first instance to make rigorous analytical calculations for the plane Ising models of a ferromagnet and for plane lattices filled with dimers (or diatomic molecules). In the second instance to make numerical and series expansion calculations, especially for three-dimensional systems.

Progress

Explicit calculations have been made of the free energy of a $m \times n$ plane square lattice filled with dimers in the limit $m, n \rightarrow \infty$ and m/n finite. The bulk terms proportional to mn , the boundary terms proportional to $(m+n)$, the constant terms of order unity and terms of $O(1/n^{2-\epsilon})$ are found.

For the plane Ising model explicit new formulas have been obtained for the interfacial free energy (surface tension). For all cases (square, triangular and honeycomb lattices) this vanishes as $(T_c - T)$ and appears to become independent of the direction of the interface as $T \rightarrow T_c$. Similarly the boundary free energy for both free and ferromagnetic walls has been found for these lattices. The most notable conclusion is that the boundary contributions to the specific heat anomaly diverge as $1/(T_c - T)$. This can be understood from more general arguments.

Some preliminary series calculations have been made for three dimensional models and a rather general formulation of the interfacial tension in terms of the eigenvalues of a suitable transfer kernel has been found.

PUBLICATIONS

"The Statistical Mechanics of Dimers on a Quadratic Lattice", A. E. Ferdinand, accepted for publication by J. Math. Phys., 1967.

M. E. Fisher

PUBLICATIONS - continued

"Interfacial, Boundary and Size Effects at Critical Points,"
M. E. Fisher and A. E. Ferdinand, Phys. Rev. Letters,
19, 169 (1967).

This research is supported by the Advanced Research Projects Agency

STATISTICAL MECHANICS AND THEORY OF PHASE TRANSITIONS

M. E. Fisher, Professor, Department of Chemistry

Objective

To study the foundations of statistical mechanics especially in regard to phase transitions and to develop the theory of critical phenomena.

Approach

To use rigorous mathematical analysis or accurate, convergent numerical approximations as appropriate, to elucidate the behavior of various many-body physical systems. To compare the predictions with appropriate experimental data (and other theoretical treatments).

Progress

Accurate numerical studies of the correlations and critical scattering of the Ising model above T_c were completed and analyzed theoretically. Recent neutron scattering experiments on β -brass by Als-Nielsen and Dietrich are in striking agreement with the detailed theoretical predictions (in contrast to the best previous theories).

An extensive review of the theory of equilibrium critical phenomena (but including some consideration of nonequilibrium phenomena) has been completed. The theory of the droplet model of condensation and the critical point has been extended to yield some insight into the contrasting behavior of isotropic and anisotropic ferromagnets (Ising and Heisenberg models).

Rigorous mathematical methods have been developed which yield (for the first time) upper bounds to the critical temperatures of general Ising lattices. Combined with lower bounds extended to non-isotropic interactions, rigorous expressions for T_c are found in the anisotropic limit.

Work has been done (in collaboration with Professor J. S. Langer) on the theory of critical velocities of superfluid in Helium near T_λ where the spontaneous fluctuations yield an intrinsic limitation. The theory is in agreement with the recent experiments of Reppy and collaborators.

PUBLICATIONS

Theory of Critical Fluctuations and Singularities in "Critical Phenomena," M. E. Fisher, Eds. M. S. Green & J. V. Sengers (N.B.S. 1966) p. 108-115.

"Effect of Excluded Volume on Phase Transitions in Biopolymers," M. E. Fisher. J. Chem. Phys. 45, 1469-1473 (1966).

M. E. Fisher

PUBLICATIONS - continued

"On the Dimer Solution of Planar Ising Models," M. E. Fisher,
J. Math. Phys. 7, 1776-1781 (1966).

"Theory of Critical Point Scattering and Correlations I The Ising
Model," M. E. Fisher and R. J. Burford, Phys. Rev.
156, 583 (1967).

"The Theory of Equilibrium Critical Phenomena," M. E. Fisher,
Rep. Prog. Phys. (1967).

"Magnetic Critical Point Exponents - Their Interrelation and
Meaning," M. E. Fisher, J. Appl. Phys. 38, 981 (1967).

This research is supported by the Advanced Research Projects Agency
and the National Science Foundation

I. W. Shepherd

Research Associate

C. J. Buchenauer and A. R. Evans

Research Assistants

To use optical techniques to study the electronic and vibrational properties of solids, particularly at low temperatures and as a function of applied stress.

Current projects are concerned with the effects of stress on color-center absorption spectra in alkali halides. One investigation concerns the effect of finite ion size on the strain coupling of the F-center absorption band. Another is a study of how the magnetic properties of the R center are affected by internal and applied strains.

Mr. Buchenauer has now determined the coupling of the F absorption band to cubic strain from hydrostatic pressure measurements (0 - 8 kbar at 78°K) in most of the alkali halides. Whereas in most cases the F band shows a strong dependence on lattice volume, consistent with the Mollwo-Ivey relation, the shift is found to decrease unexpectedly for those alkali halides which have large alkali ions and small halogen ions. In the most extreme case, CsF, the shift has the opposite sign. These results are explained by a model which takes account of the finite size of the alkali ions neighboring the F-center vacancy. A search for similar ion-size effects in the coupling to non-cubic strains is now in progress.

Dr. Shepherd has been studying the magnetic circular dichroism in the zero-phonon line of the R₂ band in KCl and KF. The magnitude of this effect is only about one percent of the absorption and is small because the Jahn-Teller interaction quenches the orbital angular momentum. He has found that the dichroism signal is decreased significantly by applying a uniaxial stress in addition to the magnetic field. This is explained by considering that the stress lifts the degeneracy of the ground state, thereby further quenching the angular momentum. The experimental results are in good agreement with the predictions of a perturbation calculation which assumes that the interaction of the center with the magnetic field is much smaller than the interaction with the stress. The magnitude of the internal strain in the crystal can be deduced from these results.

This research is supported by the Advanced Research Projects Agency

ELECTRONIC PROPERTIES OF DEFECTS IN IONIC CRYSTALS

D. B. Fitchen, Associate Professor, Department of Physics

L. D. Bogan, H. R. Fetterman and L. F. Stiles, Jr. Research Assistants

Objective

To identify and characterize point defects, particularly F and F-aggregate centers in alkali halides, through optical studies of their electronic (and vibronic) properties.

Approach

A detailed optical study and analysis of absorption and emission line shapes, and the effects of applied magnetic and electric fields, stress, temperature, and isotopic substitution will be initiated, with particular emphasis on the zero-phonon transitions.

Progress

F-Center Studies: Mr. Fulton completed his Ph.D. thesis on the F-center in CsF. He was able to extend the previous theories for optical line shapes to treat simultaneously spin-orbit coupling and the effect of cubic and non-cubic quantized vibrations on the excited state, to analyze and explain his extensive experimental measurements of the complex absorption band shape for this center. He also was able to correlate the experimental results on the relaxed excited states where he found several decay modes and unusual lifetime behavior.

Mr. Bogan has measured the electric-field-induced polarization of the F-center emission in several alkali halides, to try to determine the location of the "relaxed" 2s-like state. His results seem to indicate that it may lie below the 2p-like state.

Zero-Phonon Transitions: The intensive study of several F-aggregate centers with prominent zero-phonon lines in emission and adsorption have been continued. Mr. Stiles identified the F_3^+ center in NaF from the stress behavior of the resonance fluorescence line at 5456 Å and showed that its electronic structure was analogous to that of the H_3^+ molecule-ion.

Mr. Fetterman is studying the $M'(F_2^-)$ and $R'(F_3^-)$ centers in LiF. The R' appears to be a model example of the dynamic Jahn-Teller effect, with nearly all the predicted features clearly evident.

D. B. Fitchen

PUBLICATIONS

" F_3^+ Center in NaF," L. F. Stiles, Jr., and D. B. Fitchen, Phys. Rev. Letters 17, 689 (1966).

"Zero-Phonon Transitions," D. B. Fitchen, Physics of Color Centers, W. B. Fowler, ed., Academic Press (in press).

" F_3^+ Center in NaF," L. F. Stiles, Jr., M.S. Thesis, February 1967.

This research is supported by the Atomic Energy Commission

SPIN RESONANCE OF MOLECULES IN LIQUIDS AND GASES

J. H. Freed, Assistant Professor, Department of Chemistry

G. Bruno, H. Connor, M. Eastman, R. Kooser, J. Lang and D. Leniart
Research Assistants

Objective

To combine theoretical and experimental studies of spin resonance techniques in order to learn about dynamic molecular processes in liquids and gases.

Approach

To perform linewidth, saturation, ENDOR and other relaxation studies on free radicals in liquids and gases. To develop and use general theories of spin relaxation in analyzing the experiments. To explain the results in terms of dynamic molecular models.

Progress

The theoretical analysis of exchange effects on ESR saturation and ENDOR was completed, and it was found that chemical exchange and Heisenberg exchange should have identical effects as observed by these techniques. An anomalous experimental observation of splitting of some ENDOR lines (but not others) which is a function of the NMR field strength was explained in terms of a subtle combined effect of the coherence of the NMR field as well as the relaxation mechanisms. This serves also as a further confirmation of the theory. Dr. Hyde, at Varian, has almost completed a new and improved ENDOR accessory for the Cornell group. In steady-state saturation experiments it was found for the anomalously broad spectra of benzene and coronene anions that $T_1 \approx \frac{1}{2}T_2$ in support of a prediction based on the liquid-type Orbach relaxation mechanism recently proposed by Kivelson for these radicals. However, there are several important questions of accuracy in these measurements (see below).

A theoretical analysis of Heisenberg exchange in liquids has resolved the discrepancy between the two earlier theoretical treatments. Further work has suggested the possibility of using linewidth studies on Heisenberg exchange to extract information on the dynamics of interaction of the exchanging pair, i.e., whether they tend to stick together or tend readily to diffuse with respect to one another. Preliminary experimental work has begun.

J. H. Freed

Progress - continued

A theoretical framework has been developed for analyzing the effect of (a) slowed down rotational motion, and (b) higher order terms on linewidths and spin relaxation. The treatment is based on Kubo's generalized cumulant expansion techniques. One interesting prediction is that as the motion slows down, a new resonance line appears with a width equal to the inverse of the rotational correlation time.

PUBLICATIONS

"On Heisenberg Spin Exchange in Liquids," J. H. Freed, J. Chem. Phys. 45, 3452 (1966).

"Theory of Saturation and Double Resonance Effects in ESR Spectra II: Exchange vs. Dipolar Mechanisms," J. H. Freed, J. Phys. Chem. 71, 38 (1967).

"Theory of Saturation and Double Resonance Effects in ESR Spectra III: RF Coherence and Lineshapes," J. H. Freed, D. S. Leniarc and J. S. Hyde, J. Chem. Phys. (in press).

This research is supported by the Advanced Research Projects Agency, the National Institutes of Health and the Sloan Foundation

ADSORPTION, CORROSION AND CATALYSIS AT METAL SURFACES

L. H. Germer, Senior Research Associate, Department of Engineering
Physics

J. W. May and R. J. Szostak Research Associates

C. C. Chang Research Assistant

Objective

To study the interaction of gases with single crystal metal surfaces and to discover fundamental new knowledge about absorption, connection between adsorption and corrosion, and catalysis of chemical reactions.

Approach

Low energy electron diffraction (LEED) is being used to discover the structure of surfaces after gases have been adsorbed. These studies are aided by flash desorption mass spectrometry and measurements of changes in work function produced by adsorption.

Progress

The following studies have been under investigation. Study of adsorption of oxygen or of carbon monoxide is finished; the study of catalytic decomposition of NH_3 is in progress; corrosion by oxygen has been studied in some detail; new work has been completed studying oxygen adsorption; catalytic reaction of hydrogen and oxygen has been started but is not finished; changes in work function caused by adsorption is being studied by the Kelvin method.

Complex surface structures produced by adsorption of these gases upon crystal surfaces have been observed. In some cases adsorption results in rearrangement of surface metal atoms so that the topmost layer of atoms is a composite structure containing atoms of the metal as well as those of the adsorbate. In the case of co-adsorption of oxygen and carbon monoxide the oxygen is atomic and the carbon monoxide is molecular, and no reaction to form CO_2 has been observed. In the case of ammonia, NH_3 and H are separately adsorbed. Upon heating hydrogen evolved as H_2 at low temperature, and at much higher temperature the NH_3 is evolved in the form of hydrogen and nitrogen.

PUBLICATIONS

"Oxidation of the (112) Face of Tungsten," C. C. Chang and L. H. Germer, Surface Science (1967) (in press).

L. H. Germer

PUBLICATIONS - continued

"The Uncertainty Regarding Reconstructed Surfaces," L. H. Germer, Surface Science 5, 147 (1966).

"Diffraction Study of Oxygen Adsorption on a (110) Tungsten Face," L. H. Germer and J. W. May, Surface Science 4, 452 (1966).

"Coadsorption of Oxygen and Carbon Monoxide Upon a (110) Tungsten Surface," J. W. May, L. H. Germer, and C. C. Chang, J. Chem. Phys. 45, 2383 (1966).

"Adsorption of Carbon Monoxide on a Tungsten (110) Surface," J. W. May and L. H. Germer, J. Chem. Phys. 44, 2895 (1966).

"Thermally Ordered Oxygen on a Nickel Surface," L. H. Germer, J. W. May, and R. Szostak, Surface Science (in press).

"Secondary Scattering of Low Energy Electrons by Rows of Atoms," L. H. Germer and C. C. Chang, Surface Science 4, 498 (1966).

This research is supported by the Advanced Research Projects Agency, the American Iron and Steel Institute and the National Aeronautics and Space Administration

GRAIN-BOUNDARY PENETRATION OF LITHIUM INTO OXYGEN-DOPED NIOBIUM

J. L. Gregg, Professor, Department of Materials Science and Engineering

W. F. Brehm Research Assistant

Objective

To study the mechanism and kinetics of grain-boundary corrosion of niobium by lithium at temperatures in the neighborhood of 1000°C.

Approach

Bicrystals with a simple tilt about the [110] direction were grown by arc-zone melting. Oxygen was added by anodic oxidation of the surface and then diffusing the oxygen into the crystal by annealing. Specimens cut from the bicrystals were loaded into niobium tubes within stainless-steel capsules, lithium added, the capsules sealed, and then heated for various times and at several temperatures. Depth of grain-boundary attack was determined by metallographic examination and by fracturing the penetrated specimens.

Progress

Bicrystals with low oxygen contents are not attacked by lithium at temperatures up to 1200°C. Grain-boundary penetration of lithium was observed in bicrystals having tilt angles of 16° and 34° and containing over 500 ppm of oxygen at temperatures above 800°C. Depth of penetration increases as the square root of time, and approximately follows an Arrhenius temperature dependency with an activation energy of 68 kcal/mole. Hot-stage metallography showed the penetrated boundary to be liquid at test temperatures. The penetration is anisotropic; the rate of penetration parallel to the common [110] direction being greater than that perpendicular to this direction. It is postulated that the penetration of lithium results from segregation of oxygen in the boundary. A model has been developed to explain the kinetic data.

This research is supported by the Atomic Energy Commission.

RAMAN AND BRILLOUIN SCATTERING WITH GAS LASERS

P. L. Hartman, Professor, Department of Physics

F. Cirillo

Research Assistant

Objective

Measurement of elementary excitations, mainly in impurity systems.

Approach

Observation of Raman or Brillouin scattering with a gas laser source and phase sensitive detection of scattered light.

Progress

A search for Raman scattering off the ground state splitting of Li^+ in KCl and of vibrational side bands due to the ground state splitting of librating molecules, like CN^- in alkali halides, was without success. This was due to the low intensity of the He-Ne gas laser used. A study of the Brillouin scattering of a mixed system KCl-KBr is now under way.

This research is supported by the Advanced Research Projects Agency and the Office of Naval Research

ELECTRON EMISSION FROM SOLIDS DUE TO MULTI-PHOTON ABSORPTION

P. L. Hartman, Professor, Department of Physics

E. M. Logothetis Research Assistant

Objective

Exploration of a new tool for the investigation of band structure of solids.

Approach

External electron emission due to two- and three-photon absorption of laser light was studied in metals and insulators.

Progress

A study of two- and three-photon photoelectric effects in gold, stainless steel, KCl, KI and CsI was completed. Measurements of the yield as a function of incident laser intensity and retarded potential measurements established that at high incident laser powers, heating dominates the electron emission process, whereas, at lower laser powers two- and three-quantum processes cause the emission of electrons. A theory is presently being worked out.

PUBLICATIONS

"Three-Photon Photoelectric Effect in Gold", E. M. Logothetis and P. L. Hartman, Phys. Rev. Letters 18, 581 (1967).

This research is supported by the Advanced Research Projects Agency and the Office of Naval Research

X-RAY DIFFRACTION STUDIES OF TETRAPYRROLE SYSTEMS

J. L. Hoard, Professor, Department of Chemistry

D. M. Collins and B. Lee

Research Associates

Objective

To determine crystalline and molecular structure for biologically significant materials that fall into the category of cyclic tetrapyrrole systems, and to interpret the structural results in the light of other physical, chemical and biological data.

Approach

X-Ray diffraction analysis of single-crystal data constitutes the principal method of attack. Materials thus far studied have been metalloporphyrins, with special emphasis on the iron porphyrins. (The iron (II) derivative of protoporphyrin-IX is the heme group in hemoglobin and myoglobin.)

Progress

These studies demonstrate (1) that the porphine skeleton in porphyrins, structurally a planar or quasi-planar entity when unstrained, is quite readily ruffled, domed, or otherwise deformed in consequence of environmental stresses; (2) that the iron atom in the coordination group of high-spin ferric porphyrins lies well out-of-plane ($>0.30\text{\AA}$) from the four porphine nitrogen atoms to which it is bonded. Indeed, it is now clear that a high-spin ferric porphyrin is stabilized by the addition to the Fe^{3+} ion of a singly-charged, strongly-complexing, axial ligand to yield a five-coordinate, square-pyramidal, coordination group that is electrically neutral. The use of an uncharged ligand, such as a nitrogen atom of a histidine residue, yields a similar geometry for the coordination group in a high-spin ferrous porphyrin, as exemplified in the heme of deoxymyoglobin, or a derivative form of this coordination geometry in a high-spin ferric porphyrin, as in the heme of ferrimyoglobin. But in this latter case the residual field from the Fe^{3+} ion through the base of the coordination pyramid permits the weak attachment in the sixth position of a ligand such as H_2O or F^- that does not modify appreciably the coordination geometry and is incapable of triggering the transition from the high-spin to the low-spin state.

Extensive experimental data together with an approximate theory for coordination complexes of transition period cations strongly suggest that the transition of a high-spin iron porphyrin to the low-spin state should be accompanied by significant changes

J. L. Hoard

Progress - continued

in the geometry of the coordination group. In a low-spin six-coordinate porphyrin, the four porphine nitrogen atoms and the iron atom (whether ferrous or ferric iron) are expected to be essentially co-planar with Fe-N bonds that are 0.10-0.15Å shorter than the corresponding values in the high-spin porphyrin; the proven flexibility of the porphine skeleton is pertinent in this connection. (The still more drastic conformational change expected during the oxygenation of myoglobin, if the low-spin oxymyoglobin molecule has the Fe (II) atom in seven-coordination, is discussed in "Some Aspects of Heme Stereochemistry," as referenced below.) Such conformational changes are not found by the Cambridge Workers (Stryer, Kendrew, and Watson, *J. Mol. Biol.* 8, 96 (1964)) from the application of a highly approximate form of Fourier difference-synthesis to, jointly, the low-resolution X-ray data recorded from crystals of the high-spin ferrimyoglobin and of its low-spin azide derivative. A detailed analysis of their procedure (in "Some Aspects of Heme Stereochemistry") shows, however, that it corresponds only to the required first stage of approximation to the structural problem of interest, and that it can lead only to the qualitative identification of such gross changes in structure as the addition or the excision of an ion or molecule (H_2O , N_3^- , etc.). But it is also demonstrated that the analysis of the X-ray data can be carried to successively higher stages of approximation. Consequently, it has been arranged with Drs. H. C. Watson and J. C. Kendrew to get their X-ray data for three pertinent myoglobin derivatives in order that the further analysis may be carried out to decide, at least semi-quantitatively, whether important conformational changes do or do not accompany the transition of an iron porphyrin from the high-spin to the low-spin state.

PUBLICATIONS

- "Stereochemistry of Porphyrins," J. L. Hoard, in "Hemes and Hemoproteins," B. Chance, R. W. Estabrooks, and T. Yonetani, eds., Academic Press, New York (1966), pp. 9-24.
- "The Stereochemistry of the Coordination Group in an Iron (III) Derivative of Tetraphenylporphine," J. L. Hoard, G. H. Cohen, and M. D. Glick, *J. Am. Chem. Soc.* 89, 1992 (1967).
- "The Stereochemistry of the Coordination Group in Aquozinc (II) Tetraphenylporphine," M. D. Glick, G. H. Cohen, and J. L. Hoard, *J. Am. Chem. Soc.* 89, 1996 (1967).

J. L. Hoard

PUBLICATIONS - continued

"Some Aspects of Heme Stereochemistry," J. L. Hoard, in "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, eds., W. H. Freeman and Company, San Francisco (1967) (in press).

This research is supported by the Advanced Research Projects Agency and the National Institutes of Health

STEREOCHEMISTRY OF CHELATED SPECIES OF HIGHER COORDINATION NUMBERS

J. L. Hoard, Professor, Department of Chemistry

M. D. Glick and E. Huber Research Associates

J. J. Park Research Assistant

Objective

The determination of stereochemistry for discrete complexed species in which the coordination numbers of the central atoms exceed six, and the interpretation of these data in the light of other physical measurements in order to formulate the structural principles that govern the stability of such complexes. (See Hoard and Silverton, *Inorg. Chem.*, 2, 235-243 (1963) for a critical discussion of discrete eight-coordination, and E. L. Muetterties, *Quarterly Reviews*, 21, 109-194 (1967) for an excellent comprehensive review of the entire mushrooming field.).

Approach

Analysis of the X-ray diffraction data afforded by single crystals is the principal tool for the stereochemical study of complexed species that utilize the higher coordination numbers. Such complexes, with few exceptions, are stable only as chelated species, and the choice of chelating agent is of considerable moment. A particularly versatile, bidentate, chelating agent that complexes with a variety of cations to exemplify a wide range in coordination numbers is the tropolonate ion. The dominant role of multidentate chelation in dictating coordination type is to be seen in the aminopolycarboxylate complexes.

Progress

Completed work with seven-, nine-, and ten-coordinate aminopolycarboxylate chelates is exemplified in the list of publications. Prior to the present studies, all of these complexes were routinely formulated as octahedral complexes, in rather evident disregard of the constraints imposed by the continuously-jointed, multiply-branched, ring systems. The thermodynamic properties in aqueous solution of the ethylenediaminetetraacetato chelates of the lanthanide (Ln^{3+}) series of ions seem to correlate with the structural data.

The first studies of tropolono complexes near completion. Miss Park and Dr. Collins have determined the structure of the seven-coordinate tris (tropolono) monochlorotin (IV) molecule

J. L. Hoard

Progress - continued

and Dr. Huber has determined the stereochemistry of the nine-coordinate tetrakis (tropolono) monaquo thorium (IV) molecule. Of three distinctive coordination polyhedra that are theoretically and practically available for coordination number seven, the tin complex chooses the pentagonal bipyramid; rather convincing, but somewhat detailed, reasons for this choice can be advanced. The thorium complex utilizes a previously unobserved coordination polyhedron--the monocapped square antiprism--that is readily seen to be a sound choice, both sterically and from the standpoint of approximate bonding theory.

Continuing interest in still another structural field is evidenced by the chapter, "Elemental Boron and Compounds of High Boron Content: Structure, Properties, and Polymorphism," as listed under Publications.

PUBLICATIONS

- "The Crystal Structures of the Ethylenediaminetetraacetic acid Complexes of Lanthanum (III) and Terbium (III)," B. Lee, Ph.D. Thesis, Cornell University, February 1967.
- "The Structure of the Seven-Coordinate trans-1,2-Diaminocyclohexane-N,N'-tetraacetatoaquoferrate (III) Ion in Crystals of the Calcium Salt," G. H. Cohen and J. L. Hoard, J. Am. Chem. Soc. 88, 3228 (1966).
- "Stereochemistry of the Ethylenediaminetetraacetate Chelates of the Lanthanide Ln^{3+} Ions," B. Lee, M. D. Lind, and J. L. Hoard, Presented in the "Symposium on the Chemistry of the Lanthanide and Actinide Elements," 152nd Meeting of the American Chemical Society, New York, September 11-16, 1966.
- "Stereochemistry of the Binuclear Ethylenediaminetetraacetatodimolybdate (VI) Anion," M. D. Glick, J. J. Park, and J. L. Hoard, Presented at the "Ninth International Conference on Coordination Chemistry," St. Moritz, Switzerland, September 5-9, 1966.
- "Elemental Boron and Compounds of High Boron Content; Structure, Properties, and Polymorphism," J. L. Hoard and R. E. Hughes, in "The Chemistry of Boron and Its Compounds," E. A. Muetterties, ed., John Wiley and Sons, Inc., New York, 1967, pp. 25-154.

This research is supported by the Advanced Research Projects Agency and the National Science Foundation

NMR STUDIES OF THE ELECTRON SYSTEM IN METALS AND OF THE NATURE OF THE TRANSITION TO THE METALLIC STATE

D. F. Holcomb, Professor, Department of Physics

M. N. Alexander, G. P. Carver and J. A. Kaeck Research Assistants

Objective

Interest in this work is split between two distinct, although related, objectives. The first is to study properties of the electron system in simple metals, particularly at low temperatures, via the electron-nucleus magnetic coupling. The second is to study the nature of the transition from insulating to conducting behavior in systems where this transition is controlled by the level of impurity concentration.

Approach

The basic experimental information is obtained primarily from measurements of three NMR parameters, the Knight shift of the resonance frequency, the spin-lattice relaxation time, and the shape and width of the resonance line. In all systems being studied, these parameters are determined by the basic properties of the electron system - density of electron energy states, level of Fermi-Dirac degeneracy, wave functions of the conduction electrons and spin susceptibility of the electron system.

Progress

Substantial progress has been made in two areas.

(1) Low temperature nuclear spin system thermal relaxation times have been remeasured for cesium metal. It has now been ascertained that previously reported anomalous results stemmed from temperature measurement problems, and the cesium relaxation time, T_1 , is proportional to $1/T$, the typical behavior for a metal, from 300°K to 1.4°K, the limits of our measured range. Values of T_1 for the Rb^{87} spin system in rubidium metal, were also measured and a value for the product T_1T , (where T is the absolute temperature,) was found which agrees with previously measured room temperature values, provided a correction for the effect of thermal contraction on the electron density of states is included.

(2) Studies of the transition from semiconducting to metallic behavior in the SiC:N system, as a function of nitrogen concentration, have been completed. Delocalization of the electrons at about 6×10^{19} donors/cc is observed in the 6H polytype. In the cubic polytype, above 10^{20} donors/cc, the measurements show electrons in the conduction band of the SiC lattice. Sharp differences between the behavior of the Si^{29} spin system and the C^{13} spin system confirm band structure calculations by Bassani and Yoshimine and by Herman.

D. F. Holcomb

PUBLICATIONS

"Nuclear Spin Relaxation in the Cs Metal," D. F. Holcomb, J. A. Kaeck and J. H. Strange, Phys. Rev. 150, 306 (1966).

This research is supported by the Advanced Research Projects Agency
and the Army Research Office - Durham

COLOR CENTERS AND OXYGEN-CONTAINING DEFECTS IN NaF:OH^- AND NaF:O^{2-}

D. F. Holcomb, Professor, Department of Physics

M. Meistrich and A. Chandra

Research Assistants

Objective

The objective is to study photochemical processes in NaF. In particular, interest is concentrated in the types of ionization states of F-aggregate centers in NaF. These centers enter into various chemical and photochemical reactions with defects in the crystals produced by addition of OH^- ions or O^{2-} ions. The basic purpose is to assign models for the various defects observed and to follow the chemical reactions taking place.

Approach

Crystals with various concentrations of OH^- and O^{2-} impurities have been grown. Various sequences of x-ray treatment, optical bleaching, and thermal bleaching produce particular reaction products. These are studied by a variety of techniques - electron spin resonance, optical absorption in the visible, UV, and infrared ranges, luminescence and others.

Progress

One particular product of x-irradiation in oxygen-containing crystals is the substitutional ion, O_2^- . The properties of this defect have been carefully studied. Other products of the initial x-ray process in these crystals have been studied. An ESR pattern tentatively identified as arising from substitutional O^- has been observed. F center formation at room temperature depends strongly upon presence of the oxygen defects. Crystals have been grown enriched in O_2^- , which permits positive identification of oxygen defects responsible for ESR patterns.

Presence of OH^- ions plays a profound role in the formation and stability of various F-aggregate centers. Studies of the concentration of these F-aggregate centers shows that products of decomposition of OH^- act as electron acceptors, driving the F-aggregate centers toward electron deficiency.

PUBLICATIONS

"Electron Spin Resonance of the ICI^-V_k Center," M. L. Meistrich and L. S. Goldberg, Solid State Comm. 4, 469 (1966)

This research is supported by the Office of Naval Research

MACROMOLECULAR STRUCTURE

R. E. Hughes, Professor, Department of Chemistry

A. Karipides Research Associate

P. Barber, J. Bloor, R. Cella, R. Fletterick and P. Ward
Research Assistants

Objective

To study supramolecular organization and structure in macromolecular systems in a combined program of x-ray diffraction and conformational analysis.

Approach

Characterization of helix structures in macromolecules through Fourier transform analysis of x-ray diffraction data. Development of energy minimization techniques for conformational analysis. Simultaneous minimization in diffraction and conformational analyses.

Progress

Computer programs have been developed for calculating diffraction transforms for helix structures and for arbitrary arrays of helix structures. A more limited program for coiled-coil structures is being generalized. Other programs have been developed for conformational analysis of large molecules through energy minimization techniques; these include non-bonded interactions between molecules related through crystallographic symmetry operators. The programs are being tested on a number of macromolecular structures including polyethylene oxide, polypropylene oxide, polyphenyl glycidyl ether, polyepichlorohydrin, polyisopropyl acrylate, polymethyl methacrylate, sulfur and poly-L-valine. X-ray diffraction data have been recorded for all of these systems.

PUBLICATIONS

"Stereoregularity in Poly(isopropyl acrylate). I. Chain Dimensions by Viscometry and Osmometry," J. E. Mark, R. A. Wessling, and R. E. Hughes, J. Phys. Chem. 70, 1895 (1966).

"Stereoregularity in Poly(isopropyl acrylate). II. Light-Scattering Results and Intrinsic Viscosity-Molecular Weight Relationships at High Chain Extension," R. A. Wessling, J. E. Mark, E. Hamori, and R. E. Hughes, J. Phys. Chem. 70, 1903 (1966).

R. E. Hughes

PUBLICATIONS - continued

"Stereoregularity in Poly(isopropyl acrylate). III. Phase
Equilibrium Studies," R. A. Wessling, J. E. Mark,
and R. E. Hughes, J. Phys. Chem. 70, 1909 (1966).

This research is supported by the Advanced Research Projects Agency

CRYSTALLOGRAPHY OF ICOSAHEDRAL FRAMEWORK STRUCTURES: BORON AND BORIDES

R. E. Hughes, Professor, Department of Chemistry

B. Robertson Research Associate

L. T. Tai and J. Lemley Research Assistants

Objective

Single crystal x-ray diffraction studies of icosahedral framework structures in extremely complex elemental boron and boride systems. Preparation of single crystals and studies of the relationship of crystal structure to twinning, stacking faults and growth mechanisms in these refractory semiconductors.

Approach

Structure analysis of single crystals from x-ray diffractometric data. Crystal preparation and phase equilibrium studies at high temperature. Analysis of space group transformations through polytypic twinning and stacking faults.

Progress

Two new polytypic forms of the AlB_{12} structure have been prepared as single crystals and the space groups and unit cells have been related to the alpha and beta forms through polytypic twin operators. Variants of these new structures have been characterized by slightly different stacking fault distributions. The polytypic twin operations have been related to structure through an icosahedral framework derived from the structure of β -rhombohedral boron; at least two different twin mechanisms are required to explain the complex array of related structures. The precise structural accommodations required in the framework holes have not yet been determined, although a number of models are being tested. The new structural forms, tentatively designated as gamma- and delta- AlB_{12} , display the orthorhombic symmetries $P2_12_12_1$ and $P2_12_12_1$, respectively; the corresponding cell dimensions are 10.16, 16.56, 17.53 Å and 5.85, 8.27, 10.16 Å. Fourier analyses are in progress on the data from the alpha and gamma forms and data are being collected on the other forms.

R. E. Hughes

PUBLICATIONS

"Elemental Boron and Compounds of High Boron Content: Structure, Properties, and Polymorphism," J. L. Hoard and R. E. Hughes, in The Chemistry of Boron and its Compounds, ed. E. L. Meutterties, John Wiley and Sons, Inc., New York (1967).

This research is supported by the Advanced Research Projects Agency

ENVIRONMENT AND FRACTURE IN HIGH STRENGTH STEELS

H. H. Johnson, Associate Professor, Department of Materials Science
and Engineering

G. G. Hancock and L. L. Loushin Research Assistants

Objective

To characterize the possible interactions between stress and environment which lead to sub-critical crack growth and premature fracture in high strength steels. To correlate these results with metallurgical parameters.

Approach

Two separate investigations are underway:

1. The distribution of hydrogen in the microstructures of irons and steels is under study by electron microautoradiography.
2. The effect of microstructural characteristics upon conventional corrosion properties is under investigation, to see if a correlation with sub-critical crack growth susceptibility can be established.

Progress

1. A suitable electron microautoradiographic technique has been worked out, with tritium as the radioactive species. Preliminary experiments are underway; some evidence for rapid grain boundary diffusion of hydrogen in iron has been obtained.
2. Corrosion potentials have been determined for H-11 steel specimens quenched and tempered over a wide range of temperatures. To date, the results do not correlate with the increasing susceptibility to sub-critical crack growth and delayed failure which is evident at the higher strength levels.

PUBLICATIONS

"Sub-critical Crack Growth in Am 350 Steel," G. G. Hancock and
H. H. Johnson, Materials Research and Standards 6,
431 (1966).

This research is supported by the Advanced Research Projects Agency

DEFORMATION OF CRYSTALLINE SOLIDS

H. H. Johnson, Associate Professor, Department of Materials Science and Engineering

K. C. Joshi, J. W. Upp and G. A. McBean Research Assistants

Objective

To explore the role of point defects, and point defect production, in various deformation processes.

Approach

Two investigations are in progress:

1. The mechanisms of creep in AgCl are under study over a range of temperatures, stresses, and strain rates.
2. The production of point defects by cyclic plastic strain is determined by electrical resistivity measurements.

Progress

1. The study of creep in AgCl is nearing completion. It has been shown that the activation energy for high temperature creep is very close to the activation energy for anion diffusion. Structural observations are in progress.
2. A fully instrumented high frequency fatigue machine has been designed and constructed. Cyclic strain hardening curves have been determined for high purity copper and aluminum at 78°K and 300°K. The increase in electrical resistivity associated with cyclic plastic strain is under study.

PUBLICATIONS

"Interaction between a Dislocation and an Assembly of Dislocation Arrays," J. Appl. Phys. 37, 2978 (1966).

"High Frequency Fatigue of Copper," G. A. McBean, M.S. Thesis, June 1967.

This research is supported by the Advanced Research Projects Agency

IRON-57 MOSSBAUER EFFECT STUDIES

E. S. Kostiner, Assistant Professor, Department of Chemistry

Objective

To investigate the valence, site distribution and magnetic interactions of iron atoms in various oxide ferrite materials using the Mössbauer effect.

Approach

Preparation of magnetic materials by sintering reactions and by single-crystal flux growth followed by investigation of ^{57}Fe Mössbauer resonance.

Progress

A high temperature (1400°C) furnace suited for flux-crystal growth has been constructed and is in operation. Since this project has just been initiated, there is little progress to report.

This research is supported by the Advanced Research Projects Agency

A CALCULATION OF PHONON LIFETIMES FOR SOLID ARGON

J. A. Krumhansl, Professor, Department of Physics

H. D. Jones

Research Assistants

Objective

To make direct numerical computations of the scattering rate of phonons due to third order anharmonic effects, using realistic potentials for a specific material, e.g., solid argon.

Approach

The usual theory of single phonon decay rates due to anharmonic interactions leads to a conceptually simple but practically complex recipe. Starting from interatomic potentials, dispersion curves for the harmonic phonons are obtained, then the normal and umklapp collision rates are computed.

Progress

Numerical calculations have been completed over most of the Brillouin zone. The results do not show the simple algebraic dependence on either wave number or temperature that usual theories give - probably due to the fact that they are only expected to agree in the very low temperature, long wavelength, limit.

This research is supported by the Atomic Energy Commission

THE DYNAMIC STRUCTURE FACTOR OF LIQUID HELIUM FROM A QUASI-HARMONIC
PHONON VIEWPOINT

J. A. Krumhansl, Professor, Department of Physics

W. C. Kerr Research Assistants

Objective

To investigate phenomenologically and numerically the consequences of superimposing phonon excitations on an assumed reference "ground state" dependent primarily on short range correlations.

Approach

Short range pair correlations measured by x-ray or neutron diffraction and the measured phonon spectrum may be combined in an iterative theoretical expression for $S(k)$, to check whether the principal features of $S(k)$ can be explained by envisaging liquid helium as a quasi-crystal. Calculations have shown that although much of the structure can be described quite quantitatively in this manner there is an intermediate range of k (corresponding to the reciprocal of a few lattice constants) which definitely cannot be discussed in such a simplified manner. This calculation is useful in placing a limit on the role of single phonon excitations in dynamic structure of liquid helium.

Progress

Numerical calculations and a thesis have been completed. The results show a range of behavior which spans the known experimental data, but the choice of the "reference" state remains uncertain.

This research is supported by the Atomic Energy Commission

DISPLACEABLE POINT DEFECTS IN IONIC CRYSTALS

J. A. Krumhansl, Professor, Department of Physics

S. P. Bowen, M. Gomez Research Assistants

Objective

To study theoretically the static and dynamic properties of "off-center" impurities in solids. Typically, monopole impurities in cubic lattices such as Li : KCl have been considered.

Approach

Both statics and dynamics are considered. For the former a multiwell potential model is constructed for the defect ion, and symmetry methods are employed extensively to find the energy levels and states. To treat the dynamics, the method of thermodynamic Green's function is used to shed the defect coupled to the lattice.

Progress

Symmetry methods were used to classify the energy level structure for 100, 110, and 111 off site configurations. The effects of applied electric fields and uniaxial stress on the energy levels, specific heat, optical adsorption spectrum, and polarizability have been analyzed. The Green's functions for the operators describing polarizability and coupling to phonon and acoustic fields have been obtained in weak coupling approximation (to the lattice phonons). The electrical and mechanical properties for a simplified tunneling spectrum have been developed in detail.

PUBLICATIONS

- "Physical Properties of an Off-Center Impurity in the Tunneling Approximation. I. Statics," M. Gomez, S. P. Bowen, and J. A. Krumhansl, Phys. Rev. 153, 1009 (1967).
- "Theory of Displaceable Point Defects in Crystals," S. P. Bowen, M. Gomez, J. A. Krumhansl, and J.A.D. Matthew, Phys. Rev. Letters 16, 1105 (1966).

This research is supported by the Atomic Energy Commission

QUANTUM THEORY OF EQUATION OF STATE OF SOLID HYDROGEN

J. A. Krumhansl, Professor, Department of Physics

S. Y. Wu

Research Associate

Objective

To compute the cohesive energy and its volume dependence for solid molecular hydrogen at 0°K.

Approach

Solid hydrogen, together with solid He³ and He⁴, represent a limiting form of solid, sometimes referred to as "quantum solids". In these the light mass of the atoms involved leads to the situation that the atom motion kinetic energy is comparable to the interatomic potential energy. A fully quantum mechanical treatment is necessitated, and we have used the Jastrow function, cluster expanded, variational method to compute cohesive energy and its volume dependence.

Progress

An extensive study was made of both the form of the wave function (particularly the two particle part of the Jastrow wave function), and the intermolecular potentials which are currently available from other physical and chemical data. Computations were then made and these have led to values of cohesive energy and 0°K p-V dependence in good agreement with experiment over a much wider range of density than previous calculations.

PUBLICATIONS

"Equation of State of Solid Hydrogen at 0°K," J. A. Krumhansl and S. Y. Wu, Phys. Rev. Letters (1967) (in press).

HEAT PULSES IN SOLIDS, SEARCH FOR SECOND SOUND IN SOLIDS

J. A. Krumhansl and R. O. Pohl, Professor and Associate Professor,
Department of Physics

S. J. Rogers Research Associate

D. T. Channin Research Assistant

Objective

To study phonon propagation and interaction in solids using heat pulses.

Approach

Heat pulses of a duration very short compared to their time of flight through the crystal can be used for the study of phonon-defect interactions. Although the heat pulse consists of a broad spectrum of phonons, equal to the breadth of the phonon spectrum used in thermal conductivity, phonons in a heat pulse offer one great advantage: In the absence of phonon scatterers in the bulk of the crystal the front of the heat pulse is carried by phonons travelling in one crystallographic direction through the sample, namely on the straight line from emitter (heater) to detector (thermometer). The phonons travelling in different directions diffuse more slowly to the heater, due to multiple scattering on the sample surface. The attenuation of this front of the pulse (actually several pulses for the several polarizations) through defects dissolved in the sample permits a study of the attenuation of the phonons of a particular polarization and direction of propagation. Second sound in solids is of great fundamental interest and its study would shed much light on the otherwise not directly observable normal phonon-phonon collisions; heat pulse conduction by this mode of excitation is being sought.

Progress

The feasibility of the phonon-defect spectroscopy as outlined above has been demonstrated (Rogers). Pure and x-irradiated NaF were used. Channin has built a cryostat to measure pulses in crystals with tunneling impurity modes at temperatures above 0.3°K. The search for second sound in NaF has so far yielded negative results only, indicating probably that the N-processes in NaF are never strong enough to compete with the momentum destroying collisions. Clearly, crystal purity is of paramount importance for this work.

This research is supported by the Atomic Energy Commission

DEFECT VIBRATIONS IN SOLIDS

J. A. Krumhansl, Professor, Department of Physics

K. Lakatos and R. Tseng Research Assistants

Objective

To study defect vibrations in solids, with particular reference to neutron scattering.

Approach

The traditional defect vibration problem is that of mass change; this is a limited idealization. Computer calculations were carried out to compare the effect of potential changes in the theory with experiments of neutron scattering by dilute alloys, and optical studies of mixed halides.

Progress

A variety of numerical calculations were completed, particularly on Al containing heavy impurities and on alkali halides. It is found generally that the resonance characteristics of the impurity are much more sensitive to force constant changes than to mass change; this is an important practical result in view of the predilection of most theorists to do the mass defect problem because it is more tractable.

PUBLICATIONS

"Effects of Impurities on Lattice Vibrations; A Model Calculation Including Mass and Force Constant Changes; Neutron Scattering," K. Lakatos, Ph.D. Thesis, Cornell University, June 1967.

"Defect Vibrations in Alkali Halides," R. Tseng, Ph.D. Thesis, Cornell University, June 1967.

This research is supported by the Atomic Energy Commission

POLYMERIC BORON-NITROGEN COMPOUNDS

A. W. Laubengayer, Professor, Department of Chemistry

R. Maruca Research Assistant

Objective

To discover new and better methods for synthesizing mono- and di-boron substituted borazines and studying their reactions with the view of building polyborazines.

Approach

The use of various chlorinating agents to give unsymmetrically substituted borazines was investigated. Mercury (II) chloride was found to react readily with borazine to give good yields of a mixture of chlorinated borazines which could be easily separated into pure compounds.

Progress

This project has been successfully completed. The discovery of a convenient method for preparing unsymmetrically-substituted borazines opens the way for a great variety of studies which should give better understanding of borazine, which is isoelectronic and isostructural to benzene. In particular, the disubstituted borazines should be useful in building unique inorganic polymer systems.

PUBLICATIONS

"Preparation and Some Reactions of Unsymmetrically-Substituted Borazines,"
R. Maruca, P. T. Beachley, Jr., and A. W. Laubengayer, Inorg.
Chem. 6, 575 (1967).

This research is supported by the Advanced Research Projects Agency

THE DIPOLE MOMENTS OF B-TRIFLUORO-, B-TRICHLORO- AND B-TRIBROMOBORAZINE

A. W. Laubengayer, Professor, Department of Chemistry

C. W. J. Scaife Research Assistant

Objective

To evaluate the contribution of orientation, electronic and atomic polarizations to the total polarization of the three molecules.

Approach

The dielectric constants and specific volumes of dilute solutions of the three compounds in benzene and in cyclohexane were measured as a function of concentration and temperature. Refractive indices of similar dilute solutions were measured as a function of concentration. The data was used to calculate orientation, electronic, atomic and total polarizations.

Progress

This project has been successfully completed. It was concluded that these symmetrical molecules have zero dipole moments and that most of the non-zero dipole moments previously reported can be accounted for by failure to correct properly for atomic polarization.

PUBLICATIONS

"Dipole Moments of B-Trifluoro-, B-Trichloro- and B-Tribromoborazine,"
C. W. J. Scaife and A. W. Laubengayer, Inorg. Chem. 5, 1950
(1966).

This research is supported by the Advanced Research Projects Agency and
the National Science Foundation

DETERMINATION OF THE DIPOLE MOMENTS OF BORON AND CARBON BROMINATED
CARBORANES

A. W. Laubengayer, Professor, Department of Chemistry

R. Maruca Research Assistant

Objective

To make use of the data secured to arrive at verification of the charge distribution on the atoms of the boron-carbon icosahedral framework as calculated from molecular orbital theory and as indicated by the chemistry of the carboranes.

Approach

Very pure samples of known structure were provided by Dr. H. Schroeder of Olin Mathieson Chemical Corporation for study at Cornell.

Progress

This project has been successfully terminated. Dipole moment measurements of selectively substituted o- and m- carborane derivatives established that in the polar icosahedra of o-B₁₀H₁₀C₂H₂ and m-B₁₀H₁₀C₂H₂ the carbon atoms and the borons adjacent to them constitute the positive pole. This is in good agreement with theoretical considerations and other experimental evidence.

PUBLICATIONS

"The Dipole Moments of Boron and Carbon Brominated Carboranes,"
R. Maruca, H. Schroeder and A. W. Laubengayer, Inorg.
Chem. 6, 572 (1967).

This research is supported by the Advanced Research Projects Agency

STUDIES OF SUPERCONDUCTING TUNNELING BELOW 1°K

D. M. Lee, Associate Professor, Department of Physics

P. M. Tedrow Research Associate

P. Kumbhare Research Assistant

Objective

To investigate the tunneling characteristic of superconducting Cadmium-Aluminum junctions.

Approach

The tunneling characteristic of Cadmium-Aluminum junctions prepared by vacuum evaporation have been measured using an adiabatic demagnetization cryostat and a He³ refrigerator to attain temperatures below 1°K. The first derivative of the i-v curve was also obtained.

Progress

Measurements of the Cadmium energy gap are substantially in agreement with the predictions of the Bardeen-Cooper-Schneffer theory. Structure was observed both in the i-v characteristics and their first derivatives near the gap edge suggesting energy gap anisotropy in Cadmium.

PUBLICATIONS

"Electron Tunnelling in Superconducting Cd-Al₂O₃-Al Junctions,"
P. Kumbhare, Ph.D. Thesis, Cornell University, June 1967.

This research is supported by the Advanced Research Projects Agency and the National Science Foundation

STUDIES OF LIQUID AND SOLID HELIUM

D. M. Lee, Associate Professor, Department of Physics

P. M. Tedrow Research Associate

E. H. Graf, O. Heybey and J. Sites Research Assistants

Objective

To determine sound velocities of oriented single crystals of solid helium. To study the phase diagram of $\text{He}^3\text{-He}^4$ mixtures and the properties of dilute $\text{He}^3\text{-He}^4$ liquid mixtures at low temperatures. Development of $\text{He}^3\text{-He}^4$ dilution refrigerators for attainment of temperatures in the millidegree range in conjunction with the Millidegree facility.

Approach

To prepare single crystals of solid helium and measure their orientation (in the hcp phase) by optical birefringence. After determining the orientation of the crystal, the sound velocities in different directions will be measured using pulse time of flight techniques.

To use precision dielectric constant measurements and nuclear magnetic resonance techniques to determine the phase separation curve of liquid $\text{He}^3\text{-He}^4$ mixtures. To construct a $\text{He}^3\text{-He}^4$ dilution refrigerator.

Progress

Preliminary birefringence measurements have been performed on hcp solid He^4 which are in agreement with earlier Dutch measurements, but with much larger sample sizes than those obtained by the Dutch. The largest crystals were obtained below the λ point of the liquid.

Careful measurements of the dielectric constant of $\text{He}^3\text{-He}^4$ mixtures near the consolute temperature showed that the ϵ curve intersects the phase separation at its peak. The phase separation curve approached the consolute point linearly with temperature on both sides of the peak which is not the usual behavior in near critical points. However, the intersection of the ϵ curve with the phase separation curve at its peak indicates that this is not an ordinary critical point. Nuclear magnetic resonance measurements have indicated that He^3 remains soluble in concentrations of up to 6% to a temperature of absolute zero.

A $\text{He}^3\text{-He}^4$ dilution refrigerator, similar to the original machine of Hall et al has been constructed and has produced a temperature of 0.07°K .

D. M. Lee

PUBLICATIONS

"Sound Propagation in Solid Helium", D. M. Lee, Proceedings of 10th International Conference on Low Temperature Physics, Moscow, USSR, August-September, 1966.

"Optical Birefringence and Crystal Growth of Hexagonal-Close-Packed He^4 from Superfluid Helium," O. W. Heybey and D. M. Lee, Phys. Rev. Lett. 19, 106 (1967).

"Phase Separation and the Superfluid Transition in Liquid He^3 - He^4 Mixtures," E. H. Graf, D. M. Lee and J. D. Reppy, Phys. Rev. Lett. 19, 417 (1967).

This research is supported by the Advanced Research Projects Agency and the National Science Foundation

SURFACE ENERGY AND STRUCTURE OF METAL CRYSTALS

C. Y. Li, Associate Professor, Department of Materials Science
and Engineering

Objective

To measure the surface energy of alkaline metals and other light metals.

Approach

Electron diffraction technique will be used to study surface structure. The surface energy will be measured using the equilibrium shape method and the surface relaxation method. Concurrent theoretical calculations of surface energy will also be made.

Progress

This project has just been initiated and no significant progress has yet been accomplished.

This research is supported by the Advanced Research Projects Agency

METAL-CERAMIC INTERFACES

C. Y. Li, Associate Professor, Department of Materials Science and Engineering

A. H. Feingold

Research Assistant

Objective

To measure the interfacial tension and to study the kinetics of the morphological changes at the metal-ceramic interface.

Approach

Grain boundary grooving studies have been made.

Progress

The interfacial tension of the Ni-Al₂O₃ interface has been measured. The kinetics of the grooving process is found to be controlled by the coupled diffusion mechanism proposed previously. In this analysis a method for evaluating the effective diffusion coefficient has been developed.

PUBLICATIONS

"Mass Transport Analysis for Ostwald Ripening and Related Phenomena",
Che-Yu Li, J. M. Blakely, and A. H. Feingold, Acta Met.
14, 1397 (1966).

"Grain Boundary Grooving at a Solid-Solid Interface", A. H. Feingold,
J. M. Blakely, and Che-Yu Li, Proceedings of the Int. Sym.
on Special Topics in Ceramics, Alfred University (1967).

"Solid State Reactions at Nickel-Aluminum Oxide Interface",
A. H. Feingold, Ph.D. Degree June (1967).

This research is supported by the Advanced Research Projects Agency

SILVER HALIDE-AQUEOUS SOLUTION INTERFACE

C. Y. Li, Associate Professor, Department of Materials Science
and Engineering

H. A. Hoyen and J. B. Tabor

Research Assistants

Objective

To study the space charge distribution of point defects at silver halide-aqueous solution interfaces.

Approach

The existence of a space charge distribution is revealed by d.c. conductance measurements, potential relaxation studies and a.c. conductance and capacitance measurements.

Progress

The space charge potential at a silver chloride-aqueous solution interface has been measured as a function of silver ion concentrations in the solution. This space charge potential is found to influence the surface hardness of silver chloride crystals.

PUBLICATIONS

"Space Charge Distribution at the Silver Chloride-Aqueous Solution Interface", C. A. Steidel, H. A. Hoyen and Che-Yu Li, Proceedings of the Int. Sym. on Special Topics in Ceramics, Alfred University (1967).

"The Effects of Aqueous Environment on the Surface Hardening of Silver Chloride", J. B. Tabor and Che-Yu Li, Acta Met. (in press).

"Interfacial Tension of the Silver Chloride-Aqueous Solution System", J. B. Tabor, M. S. Degree February (1967).

This research is supported by the Atomic Energy Commission

STUDIES ON DEUTERIUM SOLVENT ISOTOPE EFFECTS

F. A. Long, Professor, Department of Chemistry

D. M. Goodall and E. A. Walters

Research Associates

Objective

To study the limitations of conventional theoretical treatments of deuterium solvent isotope effects and quantitatively account for variations.

Approach

To examine the influence of H_2O-D_2O mixtures on rates of slow proton transfer reactions which are quite sensitive to relative H_2O-D_2O proportions in the medium. An attempt to account for differences from theoretical behavior can be made by obtaining free energies of transfer of species from H_2O to D_2O .

Progress

Mr. Goodall has worked on the reaction of nitroalkane anions with acetic acid in H_2O-D_2O mixtures. The reaction is straightforward and its rate can be measured with high accuracy. Limitations in the conventional theoretical treatment of solvent isotope effects prevent a complete account of the observed effects and it is concluded that one must explicitly include the effect of solvent medium. This "medium effect" can be considered as non-zero values for free energy of transfer of a species from H_2O to H_2O-D_2O mixtures. Most of the requisite values can be measured independently. It was proven possible for each reaction to calculate from the data a true, medium independent value for the equilibrium constant for transfer of a deuteron from transition state to solvent water molecules. The same constant can be calculated independently from data for the reverse reaction and the two values agree well. These results show that medium effects do enter for reactions in H_2O-D_2O systems and that their neglect can lead to error. Another conclusion from these results is that they are all compatible for a direct proton transfer rather than one via an intervening water molecule.

This work is supported by the Atomic Energy Commission

MEASUREMENTS OF THE pK 's OF WEAK CARBON ACIDS USING SOLUTIONS OF DIMETHYLSULFOXIDE

F. A. Long, Professor, Department of Chemistry

J. L. Longridge

Research Associate

Objective

Tritium exchange measurements enable the rate of proton abstraction for a number of acetylenes by bases to be measured. If the pK 's of these compounds can be determined, then calculation of the rate of the reverse process (rate of proton addition to a carbon anion) could be made. This should be an extremely fast process and the technique may possibly be used as a method of measuring extremely fast reaction rates.

Approach

The pK 's of these compounds are difficult to measure accurately due to their extremely weak acidic properties. Measurements can be made in basic solutions of dimethylsulfoxide as this solvent greatly enhances the degree of ionization.

Progress

The measurements of tritium exchange for these systems have been previously made. Attempts to determine the pK 's of these compounds however, ran into experimental difficulties. This project is still at a very early stage and at the present moment the techniques for measuring the pK 's are still being evaluated.

This work is supported by the Atomic Energy Commission

STUDIES ON THE MAGNITUDE OF KINETIC ISOTOPE EFFECTS FOR HYDROGEN EXCHANGE ON AROMATIC HYDROCARBONS

F. A. Long, Professor, Department of Chemistry

J. L. Longridge and L. C. Gruen Research Associates

Objective

To measure the observed isotope effects for aromatic hydrogen exchange on the azulene nucleus, in an attempt to relate them to the degree of proton transfer in the transition state.

Approach

Kinetic studies of direct protonation of azulenes have been made using fast flow techniques. These data can be combined with measurements of deuterium and tritium exchange enabling the calculation of the relative rates of loss of the various hydrogen isotopes from the azulonium cation to a base. Reaction conditions have been varied by the use of a number of substituted azulenes and a series of bases.

Progress

Measurements have been completed for azulene, trimethylazulene, guaiazulene and guaiazulene-2-sulfonate with water as the base and also for azulene with formate and acetate ion as the base. When these data are presented in terms of ΔpK (the difference between the pK of the substrate and catalyst), a function used to express the degree of proton transfer in the transition state, then the primary kinetic isotope ratio passes through a definite maximum close to the region $\Delta pK = 0$. This is the region where the symmetrical transition state would be anticipated. The measurements provide experimental support for theoretical calculations which predicted this behavior.

PUBLICATIONS

"Hydrogen Exchange of Azulenes VI Acid-Catalyzed Dedeuteration of Azulene," L. C. Gruen & F. A. Long, Am. Chem. Soc., 89, 1287 (1967).

"Hydrogen Exchange of Azulenes VII Magnitudes of the Kinetic Isotope Effects," J. L. Longridge & F. A. Long, J. Am. Chem. Soc., 89, 1292 (1967).

This research is supported by the Atomic Energy Commission

A CARBON-ACID ACIDITY FUNCTION SCALE

F. A. Long, Professor, Department of Chemistry

M. T. Reagan

Research Associate

Objective

To establish a carbon-acid acidity function for perchloric and sulfuric acid solutions. This function is of particular interest as it refers to a proton transfer where both the base and the conjugate acid are minimally hydrogen bonded to the solvent, in contrast to other functions already established.

Approach

The protonation of a number of suitable carbon bases in $\text{HClO}_4\text{-H}_2\text{O}$ and $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ solutions of varying concentrations in order to establish an "overlap" procedure for determining the "acidity" of the HClO_4 and H_2SO_4 solutions.

Progress

A number of substituted azulenyl diaryl ethylenes and aromatic polyethers were found to be satisfactory indicators which gave adequate overlap. This study has now been successfully concluded and a carbon acidity function determined for the acids 0 - 70% aqueous H_2SO_4 and 0 - 50% HClO_4 .

This work is supported by the Atomic Energy Commission

STUDIES ON THE NATURE OF THE PROTONATION OF AZULENE-1-CARBOXYLIC ACID

F. A. Long, Professor, Department of Chemistry

J. L. Longridge

Research Associate

Objective

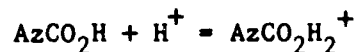
Previous measurements on this system prove ambiguous, being unable to distinguish whether protonation occurred on the carbon ring or the side chain.

Approach

The system was thoroughly re-investigated. The measurements were confused due to the decarboxylation of the compound in acid solution. Allowance had to be made for this and many of the measurements had to be repeated. In addition, further independent measurements had to be made to support the conclusions.

Progress

The nature of the decarboxylation reaction has proved to be important in characterizing the protonation. The variation of the decarboxylation rate with acidity is characteristic of a salt effect though there are marked decreases in reaction rate both in dilute and concentrated acid solutions. The dilute acid decarboxylation is clearly dependent on hydrogen ion concentration and measurements have shown that this is not due to the dissociation to the anion. It is believed to be associated with the process.



In concentrated acid, the decrease in rate is also associated with acidity and the process can be understood in terms of formation of the carbon protonated form which is stable.



Numerous investigations have been made using UV spectroscopy, NMR, conductivity and tritium exchange in order to establish that the interpretation of the kinetic data and protonation is correct.

This research is supported by the Atomic Energy Commission

ULTRA-FAST SPECTROSCOPY

H. Mahr, Associate Professor, Department of Physics

G. Ruff Research Associate

Objective

Study of fast relaxation processes and lifetimes of excitations in solids and liquids below 10^{-10} seconds duration.

Approach

Use of a mode locked laser source producing a train of spikes of 10^{-11} to 10^{-13} seconds duration. Measurement of the duration of scattering or luminescence from a laser excited sample by measuring the spatial width of the pulses. Methods using Michelson type interferometers with variable delay in one beam for low light intensities will be developed.

Progress

The mode locked laser system, a Nd glass rod, Q-switched by a Kodak 9470 dye has been assembled and is ready for tests.

This research is supported by the Advanced Research Projects Agency and the Office of Naval Research

PARAMETRIC LIGHT GENERATORS AND AMPLIFIERS

H. Mahr, Associate Professor, Department of Physics

D. Magde Research Assistant

Objective

Extension of tuneable laser sources into the visible. Study of parametric interactions in detail. Study of parametric amplification of incoherent light.

Approach

Pumped by a short powerful laser pulse parametrically generated radiation is observed collinear with the pump beam.

Progress

A quantitative study of parametric interaction was made in ADP. Tuneable output was observed from 4400Å to 10000Å. Good agreement of the results with theory was established.

It was found that the short coherence length of the interaction was a major cause for the small output that was seen.

PUBLICATIONS

"A Study in ADP of Spontaneous Parametric Interaction Tuneable from 4400Å to 16000Å," D. Magde and H. Mahr, Phys. Rev. Letters 18, 905 (1967).

This research is supported by the Advanced Research Projects Agency and the Office of Naval Research

STIMULATED RAMAN SCATTERING

H. Mahr, Associate Professor, Department of Physics

G. Ruff Research Associate

S. Abbi Research Assistant

Objective

Use of the stimulated Raman effect in liquids and solids for the generation of lattice vibrations.

Approach

Study of the Stokes light properties coupled with studies of vibrational state of the medium by probe beams.

Progress

The measurement of Raman Stokes intensities in various cell lengths of Nitro-benzene and Benzene and in two successive cells of both liquids as a function of incident laser power was finished.

PUBLICATIONS

"Stimulated Raman Emission and Self-Focusing of a Laser Beam in Non-Linear Media," S. Abbi, M.S. Thesis, Cornell University, June 1967.

This research is supported by the Advanced Research Projects Agency and the Office of Naval Research .

RESEARCH IN TRACE ANALYSIS

G. H. Morrison, Professor, Department of Chemistry

F. Tera Research Associate

E. Berkey, T. Kashuba and S. Peterson Research Assistants

Objective

To investigate modern instrumental techniques of trace analysis and to apply them to the study of high purity solid state materials.

Approach

Research on the fundamental aspects, optimization, and application of the following techniques: activation analysis, spark source mass spectrometry, emission spectroscopy, flame emission and atomic absorption spectrometry, chemical separations.

Progress

A study of the distribution of errors in spark source mass spectrometry has suggested a number of modifications of techniques resulting in a significant improvement in the quantitative results attainable. Effective computer programs have been developed to rapidly process and refine the spectral data. The milliprobe aspect of spark source mass spectrometry has been investigated and a system devised for the study of the distribution of trace elements in metals. The method has been applied to the study of the distribution of trace elements in iron meteorites and has permitted an evaluation of terrestrial contamination of "finds".

The study of isotopic ion exchange for the rapid removal of interfering matrices in activation analysis has been extended to the determination of trace impurities in magnesium employing mixed solvents. A comprehensive study has been made of the cation exchange behavior of 29 elements in the acetone-water-hydrochloric acid system.

Analytically useful atomic spectra of elements which form refractory oxides in flames have been observed in oxyhydrogen flames by forced aspiration of organic solutions at above normal rates. Optimum flame conditions and emission sensitivity parameters have been determined for the rare earths and many of the Group III, IV and V elements. Among the advantages demonstrated are: sensitivities which are highly competitive with other flames, elimination of carbon deposition and burner clogging, and the ability to analyze solutions of unusually high salt content without salt deposition.

G. H. Morrison

PUBLICATIONS

"Oxyhydrogen Flame Excitation of Refractory Elements", R. K. Skogerboe, A. T. Heybey, and G. H. Morrison, Anal. Chem., 38, 1821 (1966).

"Distribution of Trace Elements in Smithonia Iron Meteorite by Spark Source Mass Spectrometry", E. Berkey and G. H. Morrison, Proceedings of Symposium on Origin and Distribution of the Elements, International Association of Geochemistry and Cosmochemistry, Paris, May 1967.

This research is supported by the Advanced Research Projects Agency and the National Science Foundation

MASS SPECTROGRAPHIC STUDY OF ULTRA-TRACE ELEMENTS IN BIOLOGICAL MATERIALS

G. H. Morrison, Professor, Department of Chemistry

P. K. Hon and A. Bedrosian Research Associates

C. Evans Research Assistant

Objective

To investigate the feasibility of spark source mass spectrometry for the determination of ultratrace elements in biological materials.

Approach

Both direct and indirect methods are being investigated involving blending of the biological sample or its dry ash with high purity graphite followed by mass spectrographic measurement.

Progress

Spectral interferences arising from the fragmentary organic ions formed in the direct sparking of biological materials has made qualitative identification difficult and quantitative measurement impossible for many elements. The problem has been solved by preceeding the mass spectrographic measurement with a dry ashing step. A low temperature dry ashing technique was employed based on microwave excitation in a low pressure oxygen atmosphere. This approach minimizes both contamination and loss of the trace elements.

A variety of biological materials have been examined including whole blood, kidney tumor, lung, bone and plant material. Quantitative information on 56 trace elements in a single analysis of each sample were provided in this study. Inorganic and molecular spectral interferences present some problem in the quantitative determination of some trace elements. Presently the values are limited to an error of a factor of three because of the unavailability of sensitivity factors, but efforts are being made to overcome this limitation.

PUBLICATIONS

"Improved Spectral Measurements in Spark Source Mass Spectrometry,"
R. K. Skogerboe, W. L. Harrington, and G. H. Morrison, Anal.
Chem. 38, 1408, 1966.

G. H. Morrison

PUBLICATIONS - continued

"Trace Analysis of Biological Materials by Mass Spectrometry and Isotope Dilution," G. H. Morrison, Invited Paper SM-91/69, Proceedings of Symposium on Nuclear Activation Techniques in the Life Sciences, Int. Atomic Energy Agency, Amsterdam, May 1967.

This research is supported by the National Science Foundation

THE OXYGEN-DISLOCATION INTERACTION IN TANTALUM-OXYGEN

W. S. Owen, Professor, Director, Department of Materials Science
and Engineering

K. J. Reitsma Research Assistant

Objective

To understand the macroscopic deformation effects controlled by the interaction of moving dislocations in tantalum with interstitial solute atoms. The immediate objective is to study quantitatively the Snoek and the Cottrell drags in tantalum-oxygen.

Approach

The exploration of temperature and strain-rate ranges in which evidence of Snoek or Cottrell drag can be found in alloys with controlled oxygen concentration. The deduction of the dislocation dynamical effects from data obtained by dynamical strain-aging, stress relaxation and strain-rate change experiments.

Progress

The completed work on the equilibrium Cottrell Atmosphere at zero strain-rate was a necessary preliminary to the work on moving dislocations. The experimental techniques for the study of dynamical effects have not yet been developed to a completely satisfactory stage. A number of problems of experimentation will have to be solved before the main part of the program can be undertaken. Some measurements of the force necessary to separate a dislocation from a static Snoek atmosphere have been made. It is clear that, at suitable strain-rate and temperature, measurable serrations in plastic flow should be obtained.

PUBLICATIONS

"The Equilibrium Cottrell Atmosphere and the Discontinuous Yield in Tantalum-Oxygen," C. L. Fornby and W. S. Owen, *Acta Metallurgica* 14, 1841, 1966.

This research is supported by the Advanced Research Projects Agency

THE MECHANICAL BEHAVIOR OF IRON-NICKEL-CARBON MARTENSITES AND THE DECOMPOSITION PRODUCTS

W. S. Owen, Professor, Director, Department of Materials Science and Engineering

M. J. Roberts Research Associate

J. L. Nilles and E. J. Ryan Research Assistants

Objective

To identify the deformation modes at different temperatures and strain-rates and the strengthening mechanisms involving interstitial solute in iron-nickel-carbon martensites. To test the degree to which existing theories can be used as a basis for quantitative predictions and to develop the theory where this is shown to be necessary.

Approach

The preparation of martensitic specimens of alloys containing either carbon or nitrogen which are free from retained austenite and tempering products. This requires thin wires of selected composition (24-31% nickel, 0.003 to 0.30% carbon) quenched rapidly ($>15,000^{\circ}\text{C sec}^{-1}$) from the austenite range to a temperature less than -60°C . The activation and other parameters are deduced from the following types of experiments: measurement of (1) the flow stress in tension as a function of temperature and concentration of carbon, (2) the stress increment produced by a rapid change of strain-rate, (3) the kinetics of stress relaxation at zero strain-rate, and (4) the magnitude of yield drops produced by dynamic strain-aging.

Progress

It has been shown that at a strain-rate of 10^{-4} sec^{-1} , the rate-controlling deformation process at all temperatures between -196°C and 20°C has an activation volume of less than $30b^3$ independent of the carbon concentration. This suggests that the thermal activation of Peierls kinks might be involved, but this conclusion is tentative. The athermal stress increases markedly with increase in carbon concentration and the nature of this interaction is not understood. There now is convincing evidence that at slow strain-rates the deformation between about -60°C and 20°C is controlled by a Snoek drag mechanism and at higher temperatures (up to at least 120°C) by the dragging of Cottrell atmospheres.

W. S. Owen

Progress - continued

Some experiments on the effect of short-time aging on the activation parameters have been started. Fairly large plates of martensite have been prepared from single crystals of austenite and these will be used to study the deformation modes at temperatures down to liquid helium temperature.

PUBLICATIONS

"Solid Solution Hardening and Thermally Activated Deformation in Iron-Nickel-Carbon Martensite," M. J. Roberts and W. S. Owen, accepted by Journal of the Iron and Steel Institute.

"Dynamic Aging Effects in Iron-Nickel-Carbon martensites," W. S. Owen and M. J. Roberts, Battelle Colloquium on Dislocation Dynamics, Harrison Hot Springs, May 1967.

This research is supported by the Advanced Research Projects Agency

THE MORPHOLOGY AND STRUCTURE OF MARTENSITES AND RELATED CONSTITUENTS IN IRON ALLOYS

W. S. Owen, Professor, Department of Materials Science and Engineering

G. R. Srinivasan Research Associate

F. J. Schoen Research Assistant

Objective

To determine the crystallographic features of shear transformations in iron alloys. To correlate the macroscopic features with the substructure as revealed by electron microscopy and to identify the characteristic features of the transformations by which the various structures are produced.

Approach

The transformation of single crystals of austenite of composition selected to give structures of interest. Two-surface analysis of the surface markings on prepolished specimens and of structures revealed by polishing and etching transverse sections. Study of the surface topology of transformed specimens by interferometric methods. Hot-stage microscopy. Thin film electron microscopy.

Progress

Surface martensite on transformed iron-nickel alloys has been identified and the habit "plane" and shear direction have been determined. The effects of surface preparation have been studied and the range of alloy composition (and thus M_s temperature) within which the structure can be formed has been determined.

The major morphological features of massive martensite in iron-nickel have now been measured. The shape of the primary blocks, the habit and nature of the shear of the parallel plates and the general form of the lattice-invariant shear have all been determined. It now appears that massive martensite is a degenerate form of parallel-plate self-accommodating martensite.

PUBLICATIONS

"The Structure of Martensite in Iron-22w/o Nickel with Some Carbon," W. S. Owen and G. R. Srinivasan, A.I.M.E. Los Angeles Meeting, 1967.

This research is supported by the Advanced Research Projects Agency

ELECTROCALORIC EFFECT

R. O. Pohl, Associate Professor, Department of Physics

C. T. Alexander, G. Lombardo and R. J. Rollefson Research Assistants

Objective

To study electrocaloric effects; i.e., the low temperature cooling through adiabatic depolarization. This method is of great interest for the study of very low energy motional states of impurity ions in solids, and may also become an important tool for very low temperature cooling in cases where magnetic fields must be avoided and hence adiabatic demagnetization cannot be used.

Approach

The sample, KCl with a small addition of LiCl, or NaBr with NaF, is suspended in vacuum, with thin evaporated electrodes. Temperature is measured as the applied field is altered. The temperature range between .5 and 5°K has been studied by Lombardo. Alexander's work was to refine experimental techniques for measuring small temperature changes at low temperatures, a technique very important in electrocaloric measurements.

Progress

G. Lombardo has concentrated on a detailed study of the system KCl:Li. This system is not useful for cooling purposes. Maximum cooling occurs around $T = 1.4^\circ\text{K}$ (cooling by about $.5^\circ\text{K}$, depending on the Li concentration) and decreasing drastically at lower starting temperatures. He has also studied the change of specific heat of the samples when steady electric fields are applied. These measurements together with the dielectric work on the same system recently finished (Sack and Bogardus), should permit a quantitative description of the electrocaloric effects. So far, studies on two orientations of the electric field with respect to the crystallographic axes, namely (100) and (111) have been made. No analysis is possible before results in the (110) direction are obtained. Alexander has finished his M.S. thesis by measuring the specific heat of the three Rb salts RbCl, RbBr, and RbI, which are promising host crystals for the electrocaloric effect.

PUBLICATIONS

"The Low Temperature Specific Heats of the Rubidium Halides," C. T. Alexander, M. S. Degree, Cornell University, June 1967.

This research is supported by the Advanced Research Projects Agency

PURIFICATION OF ALKALI HALIDE CRYSTALS

R. O. Pohl, Associate Professor, Department of Physics

Objective

The preparation of research material, especially KCl, needed by research groups in the Cornell Materials Science Center.

Approach

The Crystal Growing Facility of the Materials Science Center, and various optical spectrometers, particularly the spectroscopic equipment of Professors Hartman, Mahr and Pohl are used.

Progress

The residual impurities, as detected by ionic conductivity measurements, have been reduced by more than a factor of 10 compared to any other crystals of KCl seed-pulled so far. The residual impurities are no longer detectable in thermal conductivity. There may be a few parts per million Br left in the crystal, as detected by optical uv absorption.

PUBLICATIONS

"The Preparation of Pure Alkali Halide Crystals and Some of Their Properties," J. M. Peech, D. A. Bower and R. O. Pohl, J. Appl. Phys. 38, 2166 (1967).

This research is supported by the Advanced Research Projects Agency

IMPURITY MODES IN SOLIDS

R. O. Pohl, Associate Professor, Department of Physics

J. P. Harrison and V. Narayanamurti

Research Associates

R. Pompei, P. Peressini and R. Rollefson

Research Assistants

Objective

To study the changes of the vibrational spectrum of crystals, the so-called impurity modes, and their interaction with plane wave phonons. Impurity modes are of interest from a lattice dynamical point of view, because they allow a novel way of studying crystal lattices, in particular the interatomic forces in the lattice. Impurity modes also have been found to be strong phonon resonant scatterers and hence are used to study the fundamental question of phonon-defect interactions.

Approach

At the present time optical and thermal properties of alkali halides doped with small concentrations of foreign alkali or halogen ions, or anionic molecule ions, are being studied. For the optical studies a recording infrared spectrophotometer (Beckman IR7) and a recording visible -uv spectrophotometer (Cary 14) are used. For the thermal studies several cryostats covering the temperature range from .05 to 200°K are available.

Progress

Specific heat anomalies associated with low lying impurity modes (tunneling states) of monatomic and molecular defects have been studied in detail. In particular an isotope effect of the tunneling states in KCl:Li (Li^6 and Li^7) has been found. This observation provides the first direct proof that the ions are indeed tunneling between several potential minima. The shape of the anomalies has been found to depend on the defect concentration, which indicates that an interaction between the defects has become noticeable. The influence of static electric fields on the specific heat anomaly and the thermal conductivity has been studied. This Stark Effect should deepen the understanding of the tunneling states and in particular should help to decide which of the tunneling states are responsible for the phonon resonant scattering.

The very high rotational mobility of molecular impurities in solids has been established previously. A Langevin-Debye type polarizability has been found together with this rotation in measurements of the dielectric constant. This has been explained through an alignment of the permanent molecular dipoles in the electric field (Sack & co-workers). Observing this alignment by the optical dichroism of the near infrared stretching vibration of the molecules is presently

R. O. Pohl

Progress - continued

being tried. The reason for studying molecular impurities in connection with an investigation of impurity modes is that the impurity modes connected with the molecular impurities can easily be studied because they show up as sidebands on the molecular stretching vibrations. Much of our understanding of the impurity modes connected with monatomic impurities has been obtained in this way.

The influence of in-band resonances on the thermal conductivity in mixed alkali halides has been studied extensively over the last few years. This work is nearing completion. It was found that thermal conductivity measurements and measurements of the far infrared absorption are complementary tools: weakly damped resonances are observed only in the IR, strongly damped ones only in thermal conductivity.

PUBLICATIONS

- "Thermal Conductivity in Sodium Chloride Crystals Containing Silver Colloids", J. M. Worlock, Phys. Rev. 147, 536 (1966).
- "Rotational Degrees of Freedom of Molecules in Solids, I. The Cyanide Ion in Alkali Halides", W. D. Seward and V. Narayanamurti, Phys. Rev. 148, 463 (1966).
- "Rotational Degrees of Freedom of Molecules in Solids, II. The Nitrite Ion in Alkali Halides", V. Narayanamurti, W. J. Seward, and R. O. Pohl, Phys. Rev. 148, 481 (1966).
- "Study of Localized Excitations Caused by Point Defects Using Thermal Conductivity, NATO Advanced Study Institute, Cortina d'Ampezzo, Italy, 1966, an Elementary Excitation and their Interaction in Solids, p. VIII. 1. Istituto Documentazione Associaz. Mercaunica Italiana, Milano, G. F. Nardelli, ed.
- "Use of Specific Heat and Thermal Conductivity Measurements for the study of Lattice Vibrations", R. O. Pohl, Physikertagung Munich 1966, Stuttgart, B. G. Tuebner, Germany Physical Society, ed. pg. 373.
- "Thermal Conductivity in Mixed Alkali Halides: KCl:Li and KBr:Li". F. C. Baumann, J. P. Harrison, R. O. Pohl and W. D. Seward Accepted by Phys. Rev., July 1967.
- "The Effect of Boundaries and Isotopes on the Thermal Conductivity of LiF", P. D. Thacher, Phys. Rev., 156, 975 (1967).

This work is supported by the Atomic Energy Commission

MASS SPECTROMETRIC STUDIES OF HIGH TEMPERATURE VAPORIZATION PROCESSES

R. F. Porter, Professor, Department of Chemistry

R. Yamdagni and C. Pupp Research Associates

Objective

To determine by mass spectrometric techniques heats and free energies of formation of high temperature species.

Approach

The high temperature vaporization behavior of a condensed material is studied mass spectrometrically. The sample is heated in a Knudsen cell and the effusing vapors are ionized by electron impact. From the positive ion spectrum, the molecular species in the vapor are identified and heats of vaporization are evaluated from the temperature coefficient for the process.

Progress

The vaporization behavior of $\text{BaTiO}_3(\text{s})$ and $\text{BaWO}_4(\text{s,l})$ have been investigated. BaWO_4 evaporated by at least two processes: decomposition to $\text{BaO}(\text{g})$ and tungsten oxides and by a simple process to form $\text{BaWO}_4(\text{g})$ molecules. Elemental selenium evaporated as the molecules Se_2 , Se_5 , Se_6 , Se_7 and Se_8 . The heats of vaporization of these species at 625°K are 22.8, 23.1, 20.0, 20.2 and 21.6 kcal/mole, respectively.

This research is supported by the Advanced Research Projects Agency, the Xerox Corporation and the Air Force Cambridge Research Laboratory

HIGH TEMPERATURE BORON CHEMISTRY, PHOTOCHEMISTRY OF BORAZINE

R. F. Porter, Professor, Department of Chemistry

G. H. Lee and L. Barton

Research Associates

M. Bellay, D. Betowski, M. Chakravorty, F. Grimm, A. Kaldor, M. Nadler,

M. Neiss, J. Solomon and E. Yeung

Research Assistants

Objective

To study the chemistry of high temperature species containing boron.

Approach

Species produced in high temperature reactions are identified mass spectrometrically. The thermodynamic and kinetic stability of these species are then determined. Spectroscopic and electron diffraction techniques are used to establish molecular structures. Photolysis experiments are conducted by irradiating a boron compound with radiation in the region between 1800 and 2000 Å.

Progress

Structural data have been obtained for B-H, $H_2B_2O_3$ and $H_3B_3O_3$. Work is near completion on the photochemical oxidation of diborane. Experiments on the photolysis of borazine in the presence of NH_3 , H_2O and simple alcohol indicate that B-mono-substituted borazine derivatives are formed as products.

PUBLICATIONS

"Photochemistry of Borazine: Preparation of B-monohydroxyborazine, Diborazinyl-Ether and B-monoaminoborazine," G. H. Lee and R. F. Porter, *Inorg. Chem.* 6, 648 (1967).

"Boroxine: A Simplified Preparation," L. Barton, F. A. Grimm and R. F. Porter, *Inorg. Chem.* 5, 2076 (1966).

"On the Spectrum of BH in the Near Ultraviolet," J.W.C. Johns, F. A. Grimm and R. F. Porter, *J. Mol. Spectry*, 22, 435 (1967).

"Gaseous Boroxine: Mechanism of Reaction with Boron Trihalides," M. Nadler and R. F. Porter, *Inorg. Chem.* 6, 1192 (1967).

R. F. Porter

PUBLICATIONS - continued

"Mass Spectrometric Study of the Photochemical Oxidation of Diborane,"
R. F. Porter and F. A. Grimm, Adv. in Chem. Series (1967).

"Photochemistry of Borazine: Preparation of B-monoalkoxyborazines,"
M. Nadler and R. F. Porter, Inorg. Chem., August (1967).

This research is supported by the Advanced Research Projects Agency
and the Army Research Office - Durham.

SUPERFLUID CRITICAL VELOCITY AND DENSITY DETERMINATION FOR RESTRICTED GEOMETRICS

J. D. Reppy, Associate Professor, Department of Physics

R. Henkel

Research Assistant

Objective

The superfluid density in unsaturated He film will be measured for film on plates and for film on fibers. This allows restriction of the geometric from $\infty \times \infty \times D$ to $\infty \times D \times 2\pi R$ where D is the film thickness and R the radius of the fiber. The results can be compared with the results obtained in bulk superfluid.

In addition to the superfluid density results, these measurements will yield critical velocities for flow in these geometries. It is expected that the critical velocity especially near the λ point will reflect fluctuations in the superfluid order parameter.

Approach

Persistent currents will be formed in the film and the angular momentum measured by a gyroscopic technique. The superfluid density is obtained from the temperature dependence of the angular momentum.

Progress

The basic equipment for these experiments is partially complete and should be finished this summer.

PUBLICATIONS

"Temperature Dependence of Superfluid Critical Velocities Near T_2 ,"
J. R. Chow and J. D. Reppy, Phys. Rev. Letters 19, 289² (1967).

This research is supported by the Advanced Research Projects Agency and the National Science Foundation

FLOW OF QUANTUM FLUID THROUGH VARIOUS GEOMETRIES

J. D. Reppy, Associate Professor, Department of Physics

E. Smith Research Assistant

Objective

Study flow of superfluid helium through precise microgeometries. Critical velocities will be determined as a function of geometry and temperature.

Approach

The gravity flow of helium through a wide range of flow geometries will be studied. Capacitative methods have been developed which monitor liquid levels to within one micron. The various flow geometries can be easily changed so it should be feasible to survey measurements over a wide range of sizes in a reasonably short time.

Progress

During the past year there has been a detour. Some of the same methods which are being developed for the flow work were applied in an experiment determining the density of rotating helium.

This work was stimulated by the results of Andronikashvili and Tsakadze who reported an anomalous increase in the density of rotating superfluid helium. The present experiments fail to confirm the existence of this interesting effect.

PUBLICATIONS

"On The Density of Rotating He II," E. Smith, R. Walton, H. V. Bohm and J. D. Reppy, Phys. Rev. Letters 18, 637 (1967).

This research is supported by the Advanced Research Projects Agency and the National Science Foundation

THE CRITICAL POINT IN $\text{He}^3\text{-He}^4$ PHASE SEPARATION

J. D. Reppy, Associate Professor, Department of Physics

G. Watson

Research Assistant

Objective

Investigate the critical point in the $\text{He}^3\text{-He}^4$ phase separation diagram with particular emphasis given to the relation of the λ line to the peak of the separation curve.

Approach

Two capacitors are used to determine the concentration of the two phases while a third capacitor is used to monitor (pycnometrically) the total density. The λ line is detected by the thermal response of the liquid.

Progress

Preliminary results indicate that the concentrations on both branches of the phase separation curve vary linearly with temperature as the peak is approached and further that the λ line terminates at this peak with a discontinuity in slope.

PUBLICATIONS

"Phase Separation and The Superfluid Transition In Liquid $\text{He}^3\text{-He}^4$ Mixtures," E. H. Graf, D. M. Lee and J. D. Reppy, Phys. Rev. Letters 19, 417 (1967).

This research is supported by the Advanced Research Projects Agency and the National Science Foundation

SINGLE QUANTUM MEASUREMENTS IN He^2

J. D. Reppy, Associate Professor, Department of Physics

G. Kukich Research Assistant

Objective

Creation and observation of the first levels of quantized circulation for superfluid helium contained in a narrow annulus.

Approach

The angular momentum of the quantized states will be measured using a gyroscopic technique. The various states will be produced by cooling through the λ transition while rotating at the appropriate angular velocity.

Progress

A hydrostatic bearing has been designed and built. This bearing will provide a low vibration support for the cryogenic equipment and is placed in a pit below the floor level. The basic equipment for the superfluid gyro has been completed.

This research is supported by the Advanced Research Projects Agency and the National Science Foundation

FIELD IONIZATION AND FIELD EMISSION AT METAL SURFACES

T. N. Rhodin, Associate Professor, Department of Engineering Physics

E. W. Plummer

Research Assistant

Objective

To achieve a detailed interpretation on the atomic scale of metallic binding and electron emission characteristics of both "simple" and transition metals. Emphasis is placed on parameters relating the electron interaction of the adsorbent-adsorbate system to the atomic configuration of both the adsorbent and adsorbate.

Approach

The experimental approach uses an ultra-high vacuum field ion microscope which can operate at liquid hydrogen temperatures, together with special clean metal vapor sources. Binding of atoms is related to measurements of pulse-desorption of surface atoms in terms of their electron structure and surface configuration. Electron emission measured using a Faraday cup-probe which can be positioned on a single crystal plane is correlated with the adsorption process. Combination of field-ion imaging, field-desorption and field electron emission provides a unique approach to the measurement of surface parameters on the atomic scale.

Progress

The field-desorption characteristic of 8 metals on the (111), (120), (100) and (110) crystal planes of tungsten have been measured. The binding energies characteristic of specific atomic configurations have been calculated by combining these data together with information on their ionization potentials d-band electron structure and work functions.

Enhanced field emission caused by atomic adsorption has also been measured and is being analyzed in terms of a transmission-resonance mechanism. These studies provide a reliable experimental background against which recently proposed wave-mechanical representations of the electron structure of metal surfaces can be critically evaluated.

PUBLICATIONS

"Atomic Perfection and Field Emission from Tungsten (110) Surface,"
E. W. Plummer and T. N. Rhodin, Appl. Phys. Letters (1967)
(in press).

This research is supported by the Advanced Research Projects Agency

BINDING AND MOBILITY OF ATOMS AND ELECTRONS AT CRYSTAL SURFACES
(LOW ENERGY ELECTRON DIFFRACTION)

T. N. Rhodin, Associate Professor, Department of Engineering Physics

P. W. Palmberg Research Associate

R. L. Gerlach, C. J. Todd and A. Ignatjevs Research Assistants

Objective

To critically evaluate recent advances in the atomistic theory of metal and insulator surfaces relevant to (1) the role of surface imperfections on metal condensation; (2) the structure of clean surfaces of ionic crystals; (3) the atomic and electron configuration of metal surfaces resulting from the adsorption of electropositive and electronegative atoms; (4) the possible occurrence of the reconstruction of a pure metal surface; (5) the surface energy and other properties of alkali metal surfaces; (6) influence of chemical environment on the structural stability of metal surfaces; and (7) normal and superconducting electrical transport in very thin continuous films.

Approach

High purity single crystal surfaces of metals are prepared by epitaxial growth, and surfaces of insulators by cleavage at -200°C , in ultrahigh vacuum. The atomic structure and surface binding of like and unlike atoms are measured using a combination of LEED, work function, surface coverage and desorption-energy measurements. Observation of elastic scattering is used to obtain information on long range structure and of inelastic scattering to study significant features associated with characteristic energy transitions of electrons in the region of the surface associated with Auger processes, interband transitions and plasma losses.

Progress

The effect of the electron beam on alkali halides produces dissociation of the crystal surface probably by the combined production of excitons and of Auger electron transitions. Theoretical understanding of the generation of surface point defects have led to new understanding of the role of electron bombardment and surface imperfections on the epitaxial growth of fcc metals formed on cleavage surfaces of insulators in ultrahigh vacuum.

The characteristic atomic structures of the (100) Au and (100) Ag surfaces of films were determined for the first time using LEED, combined with clean single crystal surfaces produced in UHV by epitaxial techniques. A possible model for the anomalous Au (100) 1×5 surface structure which is not stabilized by contamination has been proposed.

T. N. Rhodin

Progress - continued

The influence of the adsorption of fractional monolayers of sodium on the surface structure and the work function of Ni (110) and Ni (100) surfaces has been studied in detail. On the basis of these studies the theory for the enhanced electron emission by alkali metal adsorption is being critically revised.

The dependence of dissociation rate on electron excitation of the surface of KCl has been studied with LEED in terms of multiple ionization of surface chlorine ions and electron-hole recombination at the surface. Surface defects generated by moderate irradiation are believed to consist primarily of surface vacancies.

PUBLICATIONS

- "LEED Studies of Epitaxial Growth of Silver and Gold in Ultrahigh Vacuum," P. Palmberg, T. N. Rhodin and C. J. Todd, Appl. Phys. Letters 10, 4, 122 (1967).
- "Surface Asymmetry Mechanism for Fractional Order Peaks Observed in LEED Beams from Metals," R. L. Gerlach and T. N. Rhodin, Surface Science 8, 1 (1967).
- "Low Temperature Cleavage Manipulator for LEED Apparatus," P. W. Palmberg, Rev. Sci. Instr. 38, 834 (1967).
- "Surface Structure of the Clean Au (100) and Ag (100) Surfaces," P. W. Palmberg and T. N. Rhodin, Phys. Rev. (1967) (in press).
- "Surface Dissociation of Potassium Chloride by Low-Energy Electron Bombardment," P. W. Palmberg and T. N. Rhodin, Jour. Phys. and Chem. of Solids (1967) (in press).
- "Epitaxial Growth of Gold and Silver on Magnesium Oxide Cleaved in Ultrahigh Vacuum," P. W. Palmberg, T. N. Rhodin and C. J. Todd, Appl. Phys. Letters (1967) (in press).

This research is supported by the Air Force Office of Scientific Research

SYNTHESIS OF METALLIC POLYMORPHS

A. L. Ruoff, Professor, Department of Materials Science and Engineering

C. C. Chao Research Associate

K. L. Murty Research Assistant

Objective

To synthesize metallic forms of I, Br, NH_4 , H and to study their properties at pressure if unstable or at atmospheric pressure if metastable.

Approach

Theoretical considerations show that the above materials become metallic at high pressure. They, however, are insufficient to describe the exact pressure or to give the kinetic details of the transformation. The range calculated varies from 100 kbar to 1.2 Mbar.

Progress

During the past year tremendous strides have been made in work at extreme pressures and several experiments were reproduced which helped to make the problems more familiar. These include: (1) the synthesis of diamonds (metastable); (2) the synthesis of metallic iodine (unstable). Shortly, bromine crystals will be grown and attempts made to make metallic bromine for the first time. Current pressures are to 600 kbar. A design for the pressure system for making metallic NH_4 and metallic H has been made. Should the present pressure be insufficient for obtaining the latter, preliminary plans for a new system which might reach 1-5 Mbars have also been made.

This research is supported by the Advanced Research Projects Agency

POINT DEFECTS IN SOLIDS

A. L. Ruoff, Professor, Department of Materials and Engineering

G. Stupian Research Associate

L. S. Ching, P. McCormick, H. Rao and F. Tuler Research Assistants

Objective

- (1) To measure energy of formation of vacancy in potassium;
- (2) To measure pressure dependence of diffusion in aluminum;
- (3) To measure point defect concentrations in metals during deformation in the temperature range $0.25-0.6T_m$;
- (4) To study mechanism of creep in metals in temperature range $0.25-0.6T_m$.

Approach

- (1) Lattice parameter-length change experiment;
- (2-3) Nuclear magnetic resonance - motion narrowing;
- (4) The pressure dependence of creep should provide a surprisingly clear-cut check of whether creep mechanism is diffusion-controlled in this range.

Progress

- (1) Experiments are in progress;
- (2) Results showed that aluminum powders show an anomalous line width and an anomalous motion narrowing behavior. This is apparently due to impurities. Experiments on high purity foils will be started shortly;
- (3) This experiment will be set up as soon as (2) is finished;
- (4) Experiments are in progress.

PUBLICATIONS

"High Temperature Steady-State Creep of Iron," K. L. Murty, M.S. Thesis, Cornell University, February 1967.

"Pressure Dependence of Nuclear Spin Relaxation in Aluminum Powder," F. Tuler, Ph.D. Thesis, Cornell University, February 1967.

"Two Ranges of Creep in Potassium as a Function of Temperature and Pressure," C. Kohler and A. L. Ruoff, Jour. of Materials 2, 20 (1967).

"Pressure Dependence of High Temperature Creep in Single Crystals of Indium," G. T. Chevalier, P. McCormick and A. L. Ruoff, J. Appl. Phys., October (1967).

A. L. Ruoff

PUBLICATIONS - continued

"Enhanced Diffusion During Plastic Deformation," A. L. Ruoff,
J. Appl. Phys., November (1967).

This research is supported by the Atomic Energy Commission

HIGHER ORDER ELASTIC CONSTANTS - BINDING AND THERMAL PROPERTIES

A. L. Ruoff, Professor, Department of Materials Science and Engineering

P. Ho and D. P. Dandekar Research Associates

S. Ghafelabashi, R. Larsen, R. Lincoln and K. Koliwad Research Assistants

Objective

To study details of atomic binding and the thermal properties of simple metals and simple ionic crystals. Included as related topics are equations of state calculations, stability of phases (prediction of phase transformations) and details of transformation.

Approach

Experimentally the elastic constants (second order and third order - the latter by pressure derivatives and uniaxial stress derivatives of the second order constants) of single crystals are measured ultrasonically by phase comparison. Theoretically, the pseudo-potential method is used for energy calculation of the simple metals. The thermal contributions are calculated by a quasiharmonic model or when available from inelastic neutron scattering data combined with elastic constant data.

Progress

Present experimental work in progress includes measurements on potassium which will be extended to 4°K, on BaF₂, on RbCl and RbI, and on aluminum. Single crystals of V₃Si and 70-30 FeNi are being grown. The overall experimental and theoretical progress has been considerable. A few specifics include: analysis of ultrasonic data on Na by Cook's method to obtain good second pressure derivatives of the elastic constants (a first), a calculation of the dispersion curves for sodium based on the quasiharmonic model and on elastic constants which are in superb agreement with neutron scattering results, and a thorough justification of the linear shock-velocity particle-velocity relationship (a first).

PUBLICATIONS

- "Anharmonicity in CsBr and CsI: Higher Order Elastic Constants,"
K. M. Koliwad, Ph.D. Thesis, Cornell University, February 1967.
- "Elastic Constants of Some NaCl Type Alkali Halides," R. C. Lincoln,
K. M. Koliwad and P. B. Ghate, Phys. Stat. Sol. 18, 265 (1966).

A. L. Ruoff

PUBLICATIONS - continued

- "A Comparison of the Virial Coefficients Obtained from Shock and Ultrasonic Data for Al and Cu," A. L. Ruoff, J. Phys. Chem. Sol. 28, 453 (1967).
- "Pressure Derivatives of the Elastic Constants of NaBr and KF," K. M. Koliwad, P. B. Ghatge and A. L. Ruoff, Phys. Stat. Sol. 21, 507 (1967).
- "Morse Potential Evaluation of the Second and Third Order Elastic Constants of Some Cubic Metals," R. C. Lincoln, K. M. Koliwad and P. B. Ghatge, Phys. Rev. 157, 463 (1967).
- "On the Linear Shock-velocity, Particle-velocity Relationship," A. L. Ruoff, J. Appl. Phys. November (1967).
- "The Pressure Dependence of the Elastic Constants and an Experimental Equation of State for CuF_2 ," P. S. Ho and A. L. Ruoff, Phys. Rev. September (1967).
- "A Quasiharmonic Calculation of Lattice Dynamics for Na," P. S. Ho and A. L. Ruoff, Phys. Stat. Sol. October (1967).
- "Compact Electrical Lead for High Pressure Gas Systems Operating at Low Temperatures," R. H. Martinson and R. E. Terry, Rev. Sci. Instr. August (1967).

This research is supported by the Atomic Energy Commission

ADSORPTION OF HYPERSONIC WAVES

H. S. Sack, Professor, Department of Engineering Physics

R. Edgerton and R. Hanson Research Associates

R. Auyang Research Assistant

Objective

Study of interaction of high frequency acoustic waves with phonons and point and line imperfections in crystalline solids.

Approach

Attenuation measurements in the range of 500 to 3000 Mc/s and from 4-300°K by the pulse-echo method in crystals without and with defects introduced by radiation, impurity addition or plastic deformation. Comparison with existing theory, in particular with respect to temperature dependence.

Progress

The study of LiF (hardened with small amounts of Mg) is complete. T^4 dependence is observed for all the possible modes of simple wave propagation. The difference from a T^9 dependence observed by DeKlerk in one longitudinal mode is believed due to presence of Mg. Agreement with theories at low and high T is qualitatively good. However, the effects of anisotropy do not correlate satisfactorily with the details of existing theories. Li and CN doped KCl crystals show an absorption increase at low temperature, in line with the tunneling states observed in these crystals by other measurements. This research then permits observation of the interaction of monochromatic phonons with these defects which have localized modes of vibrations.

PUBLICATIONS

"Attenuation of High Frequency Elastic Waves in LiF", R. C. Hanson, J. Phys. Chem. Sol. 28, 476, 1967.

This research is supported by the Advanced Research Projects Agency

STUDY OF DEFECTS IN CRYSTALLINE SOLIDS: TASK I PARAELECTRIC DEFECTS

H. S. Sack, Professor, Department of Engineering Physics

H. Bogardus and N. Byer Research Associates

A. Lakatos, S. Letzring, S. Share and F. Welsh Research Assistants

Objective

Study of dipolar (electric and elastic) impurities in alkali halides in relation to low temperature quantum effects (tunneling, phonon interactions, etc.).

Approach

Use of dielectric and anelastic measurements, with temperature frequency, pressure, bias electric field, uniaxial stress, and concentration as parameters.

Progress

In the system KCl + LiCl, in which the Li^+ sits off-center, anelastic measurements indicate that the Li^+ is displaced in the [111] direction. Saturation effects at low temperature (down to 0.39°K) yield a tunnel splitting energy of 0.8cm^{-1} , which agrees with approximately 24 gc/sec resonance measurements (zero field). The apparent dipoles are 2.5D (electric) and 0.07 (elastic). In general there is good agreement between the experiments and a theory based on 8 harmonic potential wells.

Hydrostatic pressure of 8Kbar reduces the electric moment by 25%, again in good agreement with theory. With high fields at low T the polarization saturates, as predicted, and the saturation value follows the anticipated dependence on orientation. The losses vary proportional to the frequency for frequencies away from resonance, but obey a more complex law near resonance. Bias uniaxial stress gives a compliance change proportional to the stress and inversely proportional to T, which has no simple theoretical explanation.

The system KCl + KCN is much more complex, in that clusters play an important role in anelastic measurements, and low and high frequency dielectric measurements show some yet unexplained differences.

PUBLICATIONS

"Symmetry of Paraelectric Defects in Alkali Halides", N. E. Byer and H. S. Sack, Phys. Rev. Letters 17, 72 (1966).

"Zero Field Splitting of Paraelectric Centers in KCl", A. Lakatos and H. S. Sack, Sol. Stat. Comm. 4, 315 (1966).

H. S. Sack

PUBLICATIONS - continued

"Low Temperature Dielectric Properties of Li^+ and CN^- Impurities in KCl at 22 - 26Gc/sec", A. I. Lakatos, Ph.D. Degree, Cornell University, February, 1967.

"Ultrasonic Velocity and Absorption in KCl Containing Li^+ and CN^- ", N. E. Byer, Ph.D. Degree, Cornell University, February, 1967.

This research is supported by the Atomic Energy Commission

STUDY OF DEFECTS IN CRYSTALLINE SOLIDS: TASK II ELECTRONIC PROPERTIES
OF SILVER HALIDE

H. S. Sack, Professor, Department of Engineering Physics

R. Laibowitz and H. Schuman Research Assistants

Objective

Study of electronic properties such as lifetime of carriers, recombination, trapping, etc., of silver halides.

Approach

Measurements of luminescence and photoconductivity excited by a variety of radiations, in particular by laser light (two photon processes).

Progress

Two-photon band to band excitation has been observed in AgCl. The free carriers thus produced behave similarly as with uv excitation. However, at low temperature, in good crystals a fine structure of the luminescence is observed which is interpreted as phonon assisted emission. The photoconductivity under laser illumination is governed by one photon processes, presumably donor ionization; neodymium as well as ruby lasers excite photoconductivity, giving an upper limit to the donor depth. In not zone refined crystals a linear luminescence is superimposed on the quadratic effect, indicating the presence of sensitizer centers; neodymium laser light is not energetic enough to activate them.

PUBLICATIONS

"Laser-Induced Luminescence and Photoconductivity in the Silver Halides,"
R. B. Laibowitz, Ph.D. Degree, Cornell University, February,
1967.

This research is supported by the Atomic Energy Commission

DEFECTS IN CRYSTALLINE SOLIDS, TASK III DISLOCATIONS IN METAL CRYSTALS

H. S. Sack, Professor, Department of Engineering Physics

Objective

A study of the motion of dislocations in annealed and plastically deformed metals as a function of crystal orientation, temperature, thermal history, etc. Main interest: Bordoni Peak.

Approach

Internal friction measurements at 1, 4000, and 40,000 kilocycles and from 4° to 400° K, on poly and single crystals under a variety of conditions. Comparison with electron microscopy investigation.

Progress

No work has been performed on this topic since July 1, 1966, except preparation of publications.

PUBLICATIONS

"Internal Friction and Electron Microscopy Studies of Magnesium: Part I - Internal Friction," R.T.C. Tsui and H. S. Sack, accepted for publication, Acta. Met., 1967.

"Internal Friction and Transmission Electron Microscopy Studies of Magnesium: Part II - Electron Microscopy," R.T.C. Tsui, accepted for publication, Acta. Met., 1967.

This research is supported by the Atomic Energy Commission

THE CHEMICALLY ACTIVATED SINTERING OF OXIDES FOR COMPOSITES

E. Scala, Professor, Department of Materials Science and Engineering

P.E.D. Morgan Research Associate

R. Penty and N. Schaeffer Research Assistants

Objective

To determine the structural and mechanical characteristics of ultra fine grain MgO and establish effect of 2nd phase particles and fibers on the statistics of rupture strength.

Approach

The hot pressing (calcintering) will be the major approach for fabrication. The diametral compression test will be used for testing and the Weibull theory is to be used for the analysis.

Progress

Translucent MgO (theoretical density) has been made having a very fine grain size ($<10\mu$) and very high rupture strengths (over 40,000 psi equivalent of transverse rupture). Preliminary composites of several types have been made to study fiber/matrix interaction and dispersion. Nickel coated graphite fibers and alumina whiskers have been incorporated with success, indicating the feasibility of the process to preparing various fiber/oxide combinations. A significant effect on the oxide fracture has been noted, specifically an increase in cleavage type fracture compared to the characteristic intergranular fracture of the polycrystalline MgO.

This research is supported by the Advanced Research Projects Agency and the Air Force Materials Laboratory

MECHANICAL PROPERTIES OF TUNGSTEN--EFFECTS OF IMPURITIES

E. Scala, Professor, Department of Materials Science and Engineering

R. Simpson and A. Shepela Research Assistants

Objective

To study the effects of the interaction of interstitial and substitutional elements in tungsten on the shear modulus, internal friction and ductile/brittle transition characteristics.

Approach

The addition of carbon by diffusion to low % rhenium/tungsten alloys permits the preparation of wires which can be used for torsion pendulum measurements of shear modulus and for internal friction studies to study the extent and type of coupling. Also the diffusion of C₁₄ in wafers of Re/W and W single crystals will be used to compare the carbon diffusion as affected by a temperature gradient.

Progress

Previous studies have demonstrated a dramatic change in shear modulus by varying the carbon content in a 3% Re/W alloy. The torsion pendulum technique has been successfully employed, but internal friction peaks for tungsten and tungsten alloys are not clearly defined. The Re-W alloys samples, both as small diameter (.060) rod and as single crystals (1/4" D) are now available.

PUBLICATIONS

"Single and Multi-Fiber Interactions in Discontinuously Reinforced Composites," D. M. Schuster, Ph.D. Thesis, Cornell University, February 1966.

"Variation of Resolved Proportional Limit with Mosaic Angle From 77°K to 973°K in Zone Refined Tungsten," R. P. Simpson, M.S. Thesis, Cornell University, February 1967.

"Effect of Carbon Additions on the Shear Modulus of Tungsten," R. Hay and E. Scala, Technical Note, J. of AIME, (in press).

This research is supported by the Advanced Research Projects Agency and the Army Research Office - Durham

EMISSION AND STRUCTURE "THE EFFECT OF ANISOTROPY OF EMISSION"

E. Scala, Professor, Department of Materials Science and Engineering

G. Autio Research Assistant

Objective

To determine the emissivity for varying graphite structures and lower.

Approach

A direct measurement of emissivity at temperatures up to 800°C in both purified hydrogen and argon atmospheres. Materials of various orientations relative to the surface were examined. X-ray patterns, photomicrographs and interference patterns are taken before and after experiments.

Progress

The experimental work has been completed. The variations in emissivity as a function of orientation for several available anisotropic materials (BN, Be, Zr) have been determined experimentally. A variation by a factor of 2 or more has been found for the basal plane (low emissivity) compared to the prismatic plane (high E). These were compared to graphite and are in generally good agreement for the relative degree of anisotropy.

This research is supported by the Advanced Research Projects Agency

A STUDY OF THE STRUCTURE OF FIELD-EVAPORATED PLATINUM SURFACES

D. N. Seidman, Assistant Professor, Department of Materials Science
and Engineering

J. Bohlen Research Assistant

Objective

To study the contrast effects produced by the field evaporation process between 4.2°K and 65°K. In addition, we will measure the activation energy for field evaporation as a function of crystallographic plane. The latter experiment will give us information on binding energies as a function of number of nearest neighbor atoms.

Approach

The temperature dependence of the evaporation field and the current-field characteristics of several important crystallographic planes will be measured as a function of temperature.

Progress

Preliminary measurements of the field sensitivity of the field evaporation rate have started and a Faraday cage for measuring ion currents from individual planes has been constructed.

This research is supported by the Advanced Research Projects Agency

A. FIELD ION MICROSCOPE STUDY OF VACANCY DEFECTS IN QUENCHED PLATINUM

D. N. Seidman and R. W. Balluffi, Assistant Professor and Professor,
Department of Materials Science and Engineering

A. S. Berger

Research Assistant

Objective

To identify the dominant vacancy type defect in quenched platinum and to identify the atomic configuration of the nucleus for any vacancy type precipitates that might form.

Approach

High purity platinum wire is gas quenched in a cryostat and the excess resistance due to the vacancies is measured at 4.2°K. A field ion microscope specimen is then prepared from this wire and the specimen is examined for vacancy type defects on the high index crystallographic planes.

Progress

Well annealed specimens of high purity platinum were imaged at 63°K. At this temperature only the atoms on the very high index crystallographic planes were resolved and it was found necessary to image at considerably lower temperatures in order to form a well developed end form. To image at low temperatures a continuous-flow-gas-shielded liquid helium cryostat was designed and constructed.

This research is supported by the Advanced Research Projects Agency

A FIELD-ION MICROSCOPE STUDY OF INTERSTITIALS PRODUCED IN PLATINUM BY PLATINUM ION BOMBARDMENT

D. N. Seidman, Assistant Professor, Department of Materials Science and Engineering

R. M. Scanlan Research Assistant

Objective

To determine the contrast effects produced by self interstitial atoms and to determine the temperature régime in which the interstitial becomes mobile.

Approach

Platinum specimens are bombarded in situ in an ultrahigh vacuum field ion microscope at 4.2 to 6°K. The contrast effects and annealing will be observed visually and photographed with the aid of an image intensification and recording system.

Progress

An ultrahigh vacuum ($\sim 10^{-10}$ torr) field ion microscope has been constructed which has a liquid helium cryostat with a temperature range from 4.2°K to room temperature. In addition, an image intensification system with a light gain of 10^4 has been constructed and is presently being tested. A heavy metal ion gun has been constructed and the first bombardments should be made shortly.

This research is supported by the Advanced Research Projects Agency

ANNEALING KINETICS OF VACANCY DEFECTS AT ELEVATED TEMPERATURES AND DISLOCATION CLIMB PHENOMENA

D. N. Seidman and R. W. Balluffi, Assistant Professor and Professor,
Department of Materials Science and Engineering

Objective

To determine the motion energies of a monovacancy and a divacancy and the binding energy of a divacancy in various face centered cubic metals.

To determine the conditions which lead to diffusion limited dislocation climb and to study asymmetry between positive and negative climb motion.

Approach and Progress

A new technique was developed for studying the annealing of supersaturated vacancy defects at elevated temperatures in gold. A wire specimen, mounted in a He-filled cryostat immersed in liquid nitrogen, was quenched and annealed as follows: (i) the resistance heated specimen was gas quenched from 700°C to an annealing temperature ($T_a = 200 - 670^\circ\text{C}$) where it was held steady for periods between 100 msec and 10 min; (ii) the specimen was finally gas quenched to 78°K. The loss of supersaturated vacancies to dislocations during (i) and (ii) was obtained from electrical resistivity measurements at 4.2°K. The temperature-time history was obtained with a precision rapid data acquisition system which: (1) recorded, in analog form, the potential drops in the resistivity measuring circuit; (2) converted the analog data into digital form and stored them in a magnetic memory unit (the maximum speed was 4000 readings sec^{-1}); (3) punched the stored data onto tape which was fed into a computer for conversion to temperature-time data. The results were found to fit a temperature dependent diffusion controlled monovacancy-divacancy annealing model to dislocations possessing a relatively high divacancy binding energy in agreement with earlier results of Ytterhus, Siegel, and Balluffi.

PUBLICATIONS

"On The Efficiency of Dislocation in Gold," D. N. Seidman and R. W. Balluffi, Phys. Stat. Sol. 17, 531 (1966).

This research is supported by the Atomic Energy Commission and the
Advanced Research Projects Agency

SURFACE STUDIES BY HIGH ENERGY ELECTRON DIFFRACTION

B. M. Siegel, Professor, Department of Engineering Physics

J. F. Menadue Research Associate

G. Riddle Research Assistant

Objective

The study of surface structure and the interaction of adsorbates on and near the surface.

Approach

High energy reflection electron diffraction using a specially built ultra high vacuum electron diffraction camera designed to quantitatively record intensities with high accuracy by scanning the diffraction pattern.

Progress

The ultra high vacuum scanning diffraction camera has been completed. Intensities can be recorded to $\pm 1/2\%$ over a 2-1/2 decade range. Resolution of the camera $\theta/\Delta\theta = 220$ for planes of 1 Å spacing where θ is the scattering angle. Investigations are in progress on the interaction of oxygen on single crystal tungsten surfaces.

Kinetics of the oxidation of thin deposits of copper have been completed. Copper films of 20 to 45 Å mean thickness were oxidized at temperatures between 50° and 200°C and oxygen pressures between 10^{-3} to 10^{-1} Torr. The activation energy was found to be 19.4 ± 2.5 kcal/mol at oxygen pressures of 1×10^{-3} Torr. Higher pressures produce reactions at a somewhat lower activation energy. It appears that the oxidation rate depends on pressure as $p^{1.5 \pm .2}$.

PUBLICATIONS

"Quantitative Reflection Electron Diffraction in an Ultra High Vacuum Camera," B. M. Siegel and J. F. Menadue, Surface Science 8, 206 (1967).

"Electron Diffraction Studies at Intermediate Energies (50 kV) in an Ultra High Vacuum Camera: Kinetics of the Oxidation of Copper Deposits," B. M. Siegel, N. Uyeda, J. Shin and J. Menadue, Proc. of Sixth Int. Cong. for Elect. Micros. I, 537 (Kyoto, 1966).

This research is supported by the Advanced Research Projects Agency and the Air Force Office of Scientific Research

AN ULTRA HIGH RESOLUTION ELECTRON MICROSCOPE

B. M. Siegel, Professor, Department of Engineering Physics

F. H. Plomp and H. Kawakatsu Research Associates

K. Vosburg, R. Hertel, G. Riddle and L. Veneklasen Research Assistants

Objective

A high resolution electron microscope will be designed and constructed which, it is anticipated, will be capable of operating at the theoretical limit of resolution of 2 Å or better.

Approach

The present instrumental limitations which set the practical working resolution of commercially available electron microscopes, such as contamination build-up, "astigmatism", and low intensity of final image will be overcome by special design features. Among these are: ultra high vacuum in the complete column, a field emission electron gun, a superconducting objective lens and image intensifier and electronic scanning and read-out of the image. Studies will be made on the nature of image contrast and the problems of making observations on biomolecular structure at resolutions of atomic dimensions by electron optical imaging.

Progress

The development program has reached its final stages with very satisfactory results. Available now are optimum design parameters for: (1) the field emission electron gun: current fluxes of 10 to 100 amps/cm² are indicated; (2) the superconducting objective lens: spherical aberration coefficients as low as $C_s = 0.6$ mm were measured on our best pole piece configurations; (3) quadrupole projector lens: focal length variable from 0.7 mm to 4 mm can be obtained with very low distortion and chromatic aberrations (lower than the best conventional axially symmetric lens).

An electronic image read-out video system is under construction. A special integrating isocan image read-out system has been designed, built and delivered by RCA.

Computer calculations of phase contrast images from single atoms and molecular configurations have been made with and without a zone plate aperture. A photographic analogue technique has been developed and used to simulate calculated phase contrast images of such molecules as a dinucleotide of guanine and cytosine. Our results indicate that we should be able to recognize atomic configurations such as the purine and pyrimidine groups with an instrument working at the limits set by the aberrations of our superconducting lens.

The program has now entered the design phase of the first model of the high resolution electron microscope.

B. M. Siegel

PUBLICATIONS

- "Spherical Aberration Coefficients of Several Experimental Superconducting Magnetic Objective Lenses," R. Kropfli, M.S. Thesis. Cornell University, September 1966.
- "The Aberrations of a Quadrupole Quadruplet Projector," K. G. Vosburg, M.S. Thesis, Cornell University, February 1967.
- "High Resolution Objective Lenses Using Superconducting Materials," M. P. Schulhof, M.S. Thesis, Cornell University, June 1967.
- "Superconducting Lens for Electron Microscopy," N. Kitamura, M. Schulhof and B. M. Siegel, Appl. Phys. Letters 8, November 1966.
- "High Resolution Objective Lenses Using Superconducting Materials," B. M. Siegel, N. Kitamura, R. Kropfli and M. Schulhof, Proc. of Sixth Int. Cong. Elec. Micros. I, 151, Kyoto, 1966.
- "Ultimate Resolution by Phase Contrast Imaging of Molecular Objects," B. M. Siegel, C. Eisenhandler and M. Coan, Proc. of Sixth Int. Cong. Elec. Micros. I, 41, Kyoto, 1966.

This research is supported by the National Science Foundation and the National Institutes of Health

METALS IN TRANSITION-METAL-OXIDES

M. J. Sienko, Professor, Department of Chemistry

G. Bouchard and J. H. Perlstein Research Assistants

Objective

To investigate the nature of the semiconductor-metal transition.

Approach

Prepare single crystals of transition-metal-oxides (e.g., WO_3 , V_2O_5 , MoO_3) containing varying amounts of alkali metal, and measure electric, magnetic and magnetic-resonance properties as a function of concentration and temperature.

Progress

$\text{Na}_x\text{V}_2\text{O}_5$ has been investigated from 1.8° to 300°K (σ , χ , R_H) and the conclusion is that the conduction process goes by a "hopping" mechanism even up to $x = 0.33$. A crystal-field model for the hopping centers has been developed.

K_xMoO_3 , red form ($\text{K}_{0.33}\text{MoO}_3$) and blue form ($\text{K}_{0.30}\text{MoO}_3$), single crystals have been grown by electrolysis and measured over a range of temperature. The blue form was found to be metallic, but p-type above 180°K. A two-carrier molecular-orbital model has been developed.

PUBLICATIONS

"Alkali Metals in Transition-Metal-Oxides," M. J. Sienko, Chem. Soc. Special Publication 22, 429 (1967).

"Some Characteristics of Sodium Titanium Bronze and Related Compounds," A. F. Reid and M. J. Sienko, Inorg. Chem., 6, 321 (1967).

"Magnetic Susceptibility of UF_3 in the Range 2-300°K," M. Berger and M. J. Sienko, Inorg. Chem., 6, 324 (1967).

"EPR Study of Mn-doped α -Zinc Silicate Crystals," H. Perkins and M. J. Sienko, J. Chem. Phys., 46, 2398 (1967).

"Scandium Titanite and Scandium Vanadite," A. F. Reid and M. J. Sienko, Inorg. Chem. 6, 521 (1967).

M. J. Sienko

PUBLICATIONS - continued

"Solid State Studies of Potassium Molybdenum Bronzes," G. H. Bouchard, J. Perlstein and M. J. Sienko, Inorg. Chem., accepted for publication, Sept. 1967.

This research is supported by the Advanced Research Projects Agency
and the Air Force Office for Scientific Research

OXYGEN-DEFICIENT TRANSITION-METAL-OXIDES

M. J. Sienko, Professor, Department of Chemistry

J. Berak, J. Gulick and J. Young Research Assistants

Objective

To investigate the nature of electrical transport and magnetic interaction in transition-metal-compounds with particular reference to the insulator-metal transition.

Approach

Single crystals are grown and their conductivity, Hall voltage, and Seebeck effect are determined as a function of temperature and oxygen-deficiency. Attempts are being made to produce the metallic state by substituting F^- for O^{2-} in WO_3 structure.

Progress

(a) Single crystals of WO_{3-x} have been grown at pressures of oxygen ranging from 1 to 10^{-13} atm. σ and R_H data indicate carrier mobility decreases with temperature for $WO_{2.9997}$ but increases for $WO_{2.995}$. Semiconductive behavior extends over WO_{3-x} ($0 < x < .02$) but no materials could be prepared in the range $.02 < x < 0.10$. With $x > 0.10$, WO_{3-x} is metallic.

(b) An argon plasma technique has been used successfully to grow metallic crystals of Sc_2O_{3-x} .

(c) WO_3 containing F substituted for O has been prepared as $K_xWO_{3-x}F_x$. The materials are metallic but have a strong EPR signal.

(d) Single crystals of Ta_2O_{5-x} have been grown by rf heating of Ta_2O_5 in Ta at $1900^\circ C$. σ , R_H , S and χ studies show metallic behavior. Only $Ta_2O_{4.73}$ could be made. Density data suggest interstitial Ta. Behavior is metallic and correlates with Mott transitions.

PUBLICATIONS

"Solid State Studies of Oxygen-Deficient Tantalum Pentoxide," D. R. Kudrak and M. J. Sienko, Inorg. Chem., 6, 880 (1967.)

M. J. Sienko

PUBLICATIONS - continued

"Chemical and Physical Studies of Oxygen-Deficient Tantalum Pentoxide,"
D. R. Kudrak, Ph.D. Degree, Cornell University, February,
1967.

**This research is supported by the Advanced Research Projects Agency
and the Air Force Office of Scientific Research**

PHASE SEPARATION IN LITHIUM-AMMONIA SOLUTIONS

M. J. Sienko, Professor, Department of Chemistry

N. Mammano Research Associate

P. Chieux Research Assistant

Objective

(a) To investigate whether the $\text{Li}(\text{NH}_3)_{4.1}$ is a compound or an eutectic and to determine its electric, magnetic, and thermal properties.

(b) To determine by DTA analysis the exact shape of the liquid-liquid coexistence curve.

Approach

To prepare, under anerobic and anhydrous conditions, solutions of lithium in liquid ammonia and measure their physical properties as a function of temperature and of composition.

Progress

A DTA setup sensitive to 0.0001 calorie has been built and calibrated. Vacuum chain equipment has been built for high purity preparation. A viscometer has been constructed in a cryogenic bath. Some superconductivity searches on $\text{Li}(\text{NH}_3)_{4.1}$ have been made - no T_c has been observed but resistivity is still decreasing at 0.38°K. An x-ray camera has been modified for liquid-nitrogen cooling.

This research is supported by the Advanced Research Projects Agency
and the National Science Foundation

EXPERIMENTAL MAGNON PHYSICS

A. J. Sievers, Assistant Professor, Department of Physics

K. Aring, B. Clayman and H. Marsh Research Assistants

Objective

To investigate the properties of magnetic excitations in crystals.

Approach

With a low frequency susceptibility bridge, a microwave source, and also far infrared spectroscopic techniques the frequency dependent magnetic susceptibilities of pure and impure magnetic crystals are measured.

Progress

The investigation of the far infrared properties of UO_2 has been completed by K. Aring and he is now investigating the far infrared properties of the rare earth orthoferrites. H. Marsh is measuring the low temperature d.c. susceptibility of rare earth doped MnF_2 antiferromagnetic crystals. The giant susceptibility peaks which are observed at low temperature are believed to be manifestations of magnetic impurity modes below the bottom of the antiferromagnetic spin wave spectrum. B. Clayman is constructing a harmonic generator for the microwave source.

PUBLICATIONS

"A Resonant Impurity Mode and the Mössbauer Effect for Europium Doped MnF_2 ," A. J. Sievers, R. W. Alexander, Jr., and S. Takeno, Solid State Comm. 4, 483 (1966).

"Thermal Conductivity and Far Infrared Absorption in UO_2 ," K. Aring and A. J. Sievers, J. Appl. Phys., 38, 1496 (1967).

This research is supported by the Advanced Research Projects Agency

FAR INFRARED PROPERTIES OF METALS

A. J. Sievers, Assistant Professor, Department of Physics

D. Drew Research Assistant

Objective

To investigate the far infrared properties of metals.

Approach

With metal foils rolled into a transmission line geometry, the frequency dependent surface resistance is measured in the far infrared spectral region.

Progress

D. Drew is measuring the far infrared properties of superconducting foils. In particular, he is studying indium and niobium and comparing these measurements with previous results on tin and lead.

This research is supported by the Atomic Energy Commission

EXPERIMENTAL PHONON PHYSICS

A. J. Sievers, Assistant Professor, Department of Physics

R. Alexander, R. Kirby and I. Nolt Research Assistants

Objective

To investigate the lattice dynamics near defects in crystal lattices.

Approach

With far infrared spectroscopic techniques the impurity induced absorption associated with defects in crystals is being studied.

Progress

Measurements of isotope shifts for gap and resonant modes have been made. As yet theoretical lattice models can not explain the small shift for gap modes or the large shift for resonant modes. I. Nolt has completed stress measurements on three lattice resonant mode systems and found that the anharmonic coupling to the lattice is different in each case. R. Alexander has measured the temperature dependence of the low frequency lattice absorptions in order to obtain more information about the anharmonic coupling parameters. He also has surveyed the complex impurity induced phonon spectra caused by rare earth ions in MnF_2 .

PUBLICATIONS

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A. J. Sievers

PUBLICATIONS - continued

"Low Lying Lattice Resonant Modes Activated by Rare Earth Impurities in MnF_2 ," A. J. Sievers and S. Takeno, Optical Properties of Ions in Crystals, H. M. Crosswhite, ed., John Wiley and Sons (1967).

"Gap Modes Induced by Cl^- and Br^- Impurities in KI," I. G. Nolt, R. A. Westwig, R. W. Alexander, Jr., and A. J. Sievers, Phys. Rev. **157**, 730 (1967).

This research is supported by the Atomic Energy Commission

ELECTRON MICROSCOPY

J. Silcox, Associate Professor, Department of Engineering Physics

J. D. Edmonds Research Associate

E. E. Pacher Research Assistant

Objective

Development and application of sophisticated electron microscope techniques.

Approach

Development of an electron velocity analyser to supplement the liquid helium stage on a Hitachi HU11A microscope.

Progress

The analyser has been rebuilt, and it has been shown that earlier results were in error. Its use as a filter lens is improving, but it has not yet reached its ultimate potential. Some further modifications to the liquid helium stage have been undertaken.

PUBLICATIONS

"75KeV Electron Scattering Spectroscopy and Electron Microscopy",
J. D. Edmonds, Ph.D. Degree, Cornell University, June 1967.

This research is supported by the Advanced Research Projects Agency

DEFECT EFFECTS IN FERROMAGNETISM

J. Silcox, Associate Professor, Department of Engineering Physics

O. N. Srivastava

Research Associate

R. H. Geiss and F. C. Schwerer

Research Assistants

Objective

To study various aspects of the effect that defects have on ferromagnetic properties. This includes the effect of dislocation distributions on the coercivity of nickel, the electrical resistivity and magnetoresistivity of nickel alloys and the low temperature magnetic transitions of the rare earth metals by low temperature electron microscopy.

Approach

(i) Dislocation distributions and Burgers vectors of single crystals of nickel are found by transmission electron microscopy. Coercivity and Bitter pattern measurements are made on the same samples.

(ii) High purity nickel is doped with group 3d transition elements and transverse and longitudinal magnetoresistance is measured.

Progress

(i) Roughly two-thirds of the necessary data (electron micrographs) has been accumulated. So far nothing particularly unexpected has been seen.

(ii) It has been shown that Kohler's rule is obeyed for any one scattering entity provided that $B=H + 4\pi M_s$ is taken as the relevant field and the resistivity extrapolated to $B=0$ is taken as the reducing resistivity. However, different scattering entities display differing magnetoresistance and a strong variation is noted in the system of 3d impurities, which is of primary concern.

(iii) Thin films of gadolinium have been successfully prepared.

PUBLICATIONS

"Magnetic Domains in Chromium Tribromide," V. Matricardi, W. G. Lehmann, N. Kitamura and J. Silcox, Proc. of the 6th Intern. Congr. of Electr. Micr., Kyoto, 1, 617 (1966).

"A Tilt and Magnetic State for Operation at Liquid Helium Temperatures," N. Kitamura, O. N. Srivastava and J. Silcox, Proc. of the 6th Intern. Congr. of Electr. Micr., Kyoto, 1, 169 (1966).

"Columnar Structure of Thin Films," R. H. Wade and J. Silcox, Proc. of the 6th Intern. Congr. of Electr. Micr., Kyoto, 1, 619 (1966).

J. Silcox

PUBLICATIONS - continued

"Small Angle Electron Scattering from Vacuum Condensed Metallic Films. I. Theory," R. H. Wade and J. Silcox, Physica Status Solidi, 19, 57 (1967).

"Small Angle Electron Scattering from Vacuum Condensed Metallic Films. II. Experiment." R. H. Wade and J. Silcox, Physica Status Solidi 19, 63 (1967).

"Electron Microscopy Observation of Ferromagnetic Domains in Chromium Tribromide," V. R. Matricardi, W. G. Lehmann, N. Kitamura and J. Silcox, J. Appl. Phys. 38, 1297 (1967).

This research is supported by the Atomic Energy Commission

HARD SUPERCONDUCTING MATERIALS

J. Silcox, Associate Professor, Department of Engineering Physics

J. F. Emerson, J. Gosselin and R. W. Rollins Research Assistants

Objective

To study the factors controlling the properties of type II superconductors. Present work is devoted to understanding the critical currents carried by the surface.

Approach

The response of a sample to a small a.c. field superimposed on a large d.c. field is measured. Transport current measurements also are made with and without superimposed induced a.c. currents.

Progress

A detailed understanding of the a.c. transition has been achieved. Good agreement with experiment has been obtained for a model in which the sheath shields a change in magnetic field up to a critical value h_c . A particular test has been to measure the response of the specimen as a function of the amplitude of the applied a.c. field at constant d.c. field. The data provide values of h_c to be compared with the theories of Abrikosov, Park and Fink and Barnes. Further data is now being accumulated by various other methods.

PUBLICATIONS

"Low Frequency Transitions and Critical Currents in the Superconducting Surface Sheath," R. W. Rollins and J. Silcox, Solid State Comm., 4, 323 (1967).

"Surface Instabilities in Type II Superconductors," R. W. Rollins and J. Silcox, Phys. Lett., 23, 531 (1966).

"The Nature of the a.c. Transition in the Superconducting Surface Sheath in Pb-2%In," R. W. Rollins and J. Silcox, Phys. Rev., 155, 404 (1967).

"The Nature of a.c. Transitions and Critical Currents in the Superconducting Surface Sheath," R. W. Rollins, Ph.D. Degree, Cornell University, February, 1967

This research is supported by the Atomic Energy Commission

OPTICAL AND ESR STUDIES OF THE R-CENTER

R. H. Silsbee, Professor, Department of Physics

G. McKinstry Research Assistant

Objective

To understand in detail the properties of the R-center in the alkali halides and to gain from this understanding further insight into the intricacies of the Jahn-Teller Effect.

Approach

To measure and interpret the stress dependence of the ESR spectrum and the Stark Effect of the zero phonon line of the R-center in KCl.

Progress

The ESR work is completed and published. The ESR is observed only in the presence of sufficiently large applied stresses which serve to stabilize a particular linear combination of the orbitally degenerate ground states. The results are interpreted in terms of a dynamic Jahn-Teller Effect. The Stark Effect has also been studied. The permanent moment of the ground state has been determined but there are some aspects of the observed signal shapes which are not yet understood.

PUBLICATIONS

"R Center in KCl: Electron-Spin-Resonance Studies of the Ground State,"
D. C. Krupka and R. H. Silsbee, Phys. Rev. 152, 816 (1966).

This research is supported by the Atomic Energy Commission

ESR OF MAGNETIC IMPURITIES IN METALS

R. H. Silsbee, Professor, Department of Physics

D. L. Cowan Research Associate

M. Huisjen Research Assistant

Objective

To understand the magnetic properties of dilute alloys of transition elements in the noble metals.

Approach

To study the line width and intensity variations of the ESR of the Cu:Mn system as a function of Mn concentration and of temperature.

Progress

Considerable understanding of the results has been achieved using a model in which the conduction electrons are strongly coupled via exchange to the Mn spin system. This model predicts the observability of transmission ESR, a prediction confirmed by experiments.

PUBLICATIONS

"Paramagnetic Resonance Transmission in Copper-Dilute Manganese Alloys,"
D. L. Cowan, Phys. Rev. Letters 18, 770 (1967).

This research is supported by the Atomic Energy Commission

EXCITED STATE ESR SPECTROSCOPY

R. H. Silsbee, Professor, Department of Physics

L. L. Chase Research Assistant

Objective

To study the ESR of excited metastable states of magnetic ions.

Approach

To use an optical-microwave double resonance technique in which optical detection is used to observe the microwave stimulation of transitions in the metastable excited states of Cr^{3+} and V^{2+} in MgO .

Progress

This project has been completed and the results are being prepared for publication. The basic properties, g, line width and hyperfine splittings, for the excited ${}^2E$ state resonances of Cr^{3+} and V^{2+} are simply interpreted in terms of known parameters for these ions if one makes reasonable assumptions concerning the internal strains in the sample. A number of additional effects concerning line shapes and relaxation times were noted and understood qualitatively in terms of interactions with other paramagnetic ions. These problems were not pursued because specimens of suitably controlled purity are not available.

PUBLICATIONS

"Paramagnetic Resonance of the ${}^2E(3d^3)$ Level of Cr and V in MgO ," L. L. Chase, Ph.D. Thesis, February 1967.

This research is supported by the Atomic Energy Commission

MICROWAVE STUDIES OF MOLECULAR IMPURITIES IN SOLIDS

R. H. Silsbee, Professor, Department of Physics

R. A. Herendeen, S. Othmer and R. Reese Research Assistants

Objective

There are two principal objectives in this project. The first is to understand in what way various molecular impurities are incorporated in a host crystal. The second is to determine the effects of dynamic interactions between the impurity and the host on the properties of the system.

Approach

Techniques used:

- (1) Analysis of ESR spectra to determine site symmetry and electron configuration of the impurity.
- (2) Use of paraelectric resonance to determine energy level structure of impurities showing electric dipole moments.
- (3) Study, using ESR monitoring, of defect reorientation induced by externally applied mechanical stress or electric fields.

Progress

An analysis of the properties of N_2^- in NaN_3 is completed and published. The N_2^- resonance is observed only at liquid He temperatures and somewhat above. The N_2^- is substitutional for the N_3^- and, because of the degeneracy of the electronic Π state of the molecule on the trigonal field at such a site, shows Jahn-Teller effect. The resonance results indicate this to be a static Jahn-Teller system. Paraelectric resonance of Li^+ in KCl (not a molecular impurity, but similar in many properties to the molecular problem) has been observed. A study of the O_2^- reorientation kinetics in KI has been completed. The temperature and stress dependence of the O_2^- reorientation rate shows reasonable agreement with theory in the range where one-phonon processes dominate, but not at higher temperatures where multiple phonon processes become important. Spectra associated with HCN^- and FCN^- in KCl have been identified and are now being interpreted.

PUBLICATIONS

"ESR Identification of an N_2^- Defect in X-irradiated Sodium Azide,"
E. Gelerinter and R. H. Silsbee, J. Chem. Phys. 45, 1703
(1966).

R. H. Silsbee

PUBLICATIONS - continued

"Fourier Transform Analysis of Hyperfine Structure in ESR," R. H. Silsbee, J. Chem. Phys. 45, 1710 (1966).

"Reorientation of O_2^- in KI at Low Temperature," R. H. Silsbee, J. Chem. Phys. Solids (in press).

This research is supported by the Atomic Energy Commission

EFFECT OF ALLOYING ELEMENTS ON THE RECOVERY BEHAVIOR OF HIGH PURITY IRON

G. V. Smith, Professor, Department of Materials Science and Engineering

P. R. Mould Research Associate

D. Fox Research Assistant

Objective

To evaluate the effects of alloying elements in substitutional solid solutions on the recovery behavior of high purity iron.

Approach

High purity alloys of iron are prepared, with a zone-refined iron base, by cold-hearth melting. After processing to 0.070" in diameter wire, the alloys are heated in hydrogen to reduce to a minimum the quantity of the interstitial elements, carbon and nitrogen. Recovery is evaluated from the change in flow stress at room temperature followed by heating at temperatures in the recovery range after plastic straining at room temperature, followed by heating at temperatures in the recovery range.

Progress

Initial studies have been made on alloys containing chromium up to 4 atomic percent and molybdenum up to 3 atomic percent. Chromium in the amount of 1% has shown only a slight effect in retarding recovery, whereas the alloys containing greater chromium as well as all of the alloys containing molybdenum have shown strain-aging, i.e., increased flow strength, rather than recovery on heating at intermediate temperatures. Chemical analysis has shown a constant level of interstitial element concentration for the iron and for the alloys.

Evaluation of the experimental results for iron have given activation energies for beginning and ending of recovery which are representative of vacancy migration and self-diffusion respectively. The addition of 1% chromium appears to increase the activation energy for vacancy formation. Similar studies of the remaining alloys are in progress.

PUBLICATIONS

"Strain-Aging and Recovery Behavior of Fe-Cr and Fe-Mo Alloys,"
P. R. Mould and G. V. Smith, Int. Symposium on the Chem. and
Phys. Properties of High Purity Iron, C.N.R.S., Paris, *Memoires
Scientifique de la Revue de Metallurgie*, September (1966).

This research is supported by the Advanced Research Projects Agency and
the American Iron and Steel Institute

EFFECT OF ALLOYING ELEMENTS ON PLASTIC FLOW OF BODY-CENTERED CUBIC IRON

G. V. Smith, Professor, Department of Materials Science and Engineering

P. R. Mould

Research Associate

J. O'Donnell and D. Fox

Research Assistants

Objective

To evaluate the effects of solid solution alloying elements and microstructure on the plastic flow of high-purity alpha iron.

Approach

Alloys of iron are prepared from zone-refined iron and alloying ingredients of high purity, which after processing to wire .070" in diameter, are further purified by heating in hydrogen. Effects of alloying elements and microstructure are evaluated by tensile tests at different temperatures. Microstructure is evaluated by optical and by thin foil transmission electron microscopy.

Progress

Recent exploratory studies have been conducted at temperatures in the range 80°-700°C on a series of chromium and molybdenum alloys, the counterpart of those being studied in the companion program on recovery, except that the base material for preparation of the alloys has been electrolytic iron rather than zone refined iron. In spite of the hydrogen purification treatment of the test materials, we have observed evidence of dynamic strain-aging, both in terms of the occurrence of serrated plastic flow (Portevin-Le Chatelier effect) and in maxima in the variation of flow stress with test temperature.

PUBLICATIONS

- "Yield and Flow Stress Increase in Zone-Refined Polycrystalline Iron During 600°C Treatment After Wet Hydrogen Purification," B. W. Christ and G. V. Smith, *Acta Met.* (1967).
- "Quench Aging, Strain Aging and Substructure in 1020 Steel," G. V. Smith and M. F. Behun, *ASTM Journal of Materials*, June (1967).
- "Comparison of the Hall-Petch Parameters of Zone Refined Iron Determined by the Grain Size and Extrapolation Methods," B. W. Christ and G. V. Smith, *Acta Met.* 15, 807 (1967).
- "Effects of Impurities on Yield and Flow Strength of Zone-Refined Iron," B. W. Christ and G. V. Smith, *Int. Symposium on the Chem. and Phys. Properties of High Purity Iron*, C.N.R.S., Paris, *Memoires Scientifique de la Revue de Metallurgie*, September (1966).

G. V. Smith

PUBLICATIONS - continued

"Preparation and Properties of Iron Single Crystals," H. H. Kranzlein,
M. S. Burton and G. V. Smith, Memoires Scientifique de la Revue
de Metallurgie (in press).

This research is supported by the Advanced Research Projects Agency and
the American Iron and Steel Institute

EFFECT OF ALLOYING ELEMENTS ON THE PLASTIC FLOW OF FACE-CENTERED-CUBIC IRON

G. V. Smith, Professor, Department of Materials Science and Engineering

D. E. Sonon and C. F. Jenkins

Research Assistants

Objective

To evaluate the role of alloying elements, particularly carbon and nitrogen, on the plastic flow of face-centered-cubic iron.

Approach

An alloy having (in weight percent) 35% Ni, 15% Cr, balance Fe, which does not transform even during plastic deformation at as low as liquid nitrogen temperature has provided a base composition from which to study the role of interstitial alloying elements in plastic deformation. Owing to complexities inherent in the Cr-Ni-Fe alloy, an additional program has been conducted with nickel-cobalt alloys.

Progress

Mr. Sonon has completed thesis research (Ph.D.) on the effects of grain size and carbon content on the strength of nickel and nickel-cobalt alloys at room and lower temperatures. The results support the view of an elastic interaction of carbon atoms with dislocations in this system, generally in conformity with the theories of Cottrell and Fleischer. Complexities in the strengthening effect of carbon in Ni-Co alloys were such that it was not possible to satisfactorily assess the effect of stacking fault energy on strengthening by carbon.

Studies have continued (Jenkins) on the 35 Ni-15 Cr-Fe alloy with particular interest in temperatures above room temperature. The results have indicated a complex interaction of solute atoms with dislocations in the temperature range 300-700°C. Deformation at the elevated temperatures resulted in serrated flow (Portevin-Le Chatelier effect), and this phenomenon is thought to depend upon interstitial content as well as on some substitutional element, probably chromium.

G. V. Smith

PUBLICATIONS

"Effect of Grain Size and Temperature on the Strengthening of Nickel and Nickel-Cobalt Alloys by Carbon During Plastic Flow,"
D. E. Sonon, Ph.D. Thesis, Cornell University, June 1967.

This research is supported by the Advanced Research Projects Agency and the American Iron and Steel Institute

NON-LINEAR OPTICAL EFFECTS

C. L. Tang, Associate Professor, Department of Electrical Engineering

T. Giallorenzi

Research Assistant

Objective

To eventually achieve continuously tunable amplification of light over a wide range of the spectrum on a continuous basis by using the optical parametric process in suitable non-linear optical crystals. Continuously tunable optical oscillators would be extremely important for studying the infrared and optical properties of materials. The immediate objective is to clarify the non-linear processes involved and to determine the physical origin of the initial fluctuations that would lead to the observed output.

Approach

Tunable optical oscillations from 0.7-2.4 microns have already been achieved by Miller at the Bell Laboratories using pulsed lasers and LiNbO_3 . The plan is to use CW Ar^+ or Kr^{++} lasers to study first just the spontaneous emission produced in the same parametric process in order to determine the physical origin of the fluctuations that initiate the process. Earlier pulsed laser results by Miller indicate that the observed output in LiNbO_3 is 10^3 times larger than present theory predicts. The gas laser results should be much more reliable. Also, it is planned to re-examine the present theory, which was developed primarily for the microwave oscillators.

Progress

This is a new project; therefore, there is little progress to report.

This research is supported by the Advanced Research Projects Agency

THEORETICAL AND EXPERIMENTAL STUDIES OF THE IONIZED RARE GAS LASERS

C. L. Tang, Associate Professor, Department of Electrical Engineering

H. R. Marantz and R. I. Rudko Research Assistants

Objective

To gain fundamental knowledge of the detailed physical processes taking place in the ionized rare gas lasers.

Approach

To calculate numerically the wave functions, life times, and transition probabilities for all the laser states in all the important rare gas ions: Ne^+ , Ar^+ , Kr^+ , Xe^+ , Kr^{++} , etc. To make detailed measurements on all the important transitions in these lasers under different discharge conditions. To determine the nature of the excitation and relaxation mechanisms in these lasers on the basis of these results.

Progress

Numerical calculations for all the important configurations in Ne^+ , Ar^+ and Kr^+ have been completed and the results are being written up for publication. Detailed spontaneous emission data for Ar^+ and Kr^+ under various conditions have been obtained. On the basis of these results, the population densities and the pumping rates of all the laser states in the Ar^+ laser have been determined. A similar analysis of the Kr^+ laser is also being made.

PUBLICATIONS

"Effects of Cascade in the Excitation of the Ar^+ Laser," R. I. Rudko and C. L. Tang, Appl. Phys. Letters 9, 41, July, 1966.

"Relative Intensities of the $5s^2P_{3/2} \rightarrow 4p^2D_{5/2}$ and the $5s^4P_{5/2} \rightarrow 4p^4D_{7/2}$ Transitions in the Ar^+ Laser," H. Marantz, R. I. Rudko and C. L. Tang, Appl. Phys. Letters 9, 409 (1966).

"Spectroscopic Studies of the Ar^+ Laser," R. I. Rudko and C. L. Tang, J. Appl. Phys. (in press).

This research is supported by the Advanced Research Projects Agency and the National Aeronautics Space Administration

MOLECULAR LASERS

C. L. Tang, Associate Professor, Department of Electrical Engineering

B. Hocker Research Assistant

Objective

To clarify the important excitation and relaxation processes in the molecular lasers such as the CO_2 and N_2O lasers.

Approach

To determine the vibrational-rotational wave functions and the transition probabilities for the important laser states in such molecules as CO_2 and N_2O . To estimate the various relaxation times for these states.

Progress

Wave functions and transition probabilities for N_2O are being calculated by Mr. Hocker, using the general procedure used previously for CO_2 . A theory for the optical analog of the transient nutation effect in CO_2 lasers was developed; the results show that the effect could be observed at 10.6μ at an intensity level $> 20 \text{ kw/cm}^2$, which can be achieved in Q-switched CO_2 lasers. The experimental apparatus to look for the effect is being assembled. The experiment is expected to yield direct information on the dipole moment corresponding to the laser transitions and on the energy-transfer rate among the rotational levels.

PUBLICATIONS

"Probabilities for Radiative Transitions Between Laser States in CO_2 ,"
H. Statz, C. L. Tang and G. F. Koster, J. Appl. Phys. 37,
4278 (1966).

"Optical Analog of the Transient Nutation Effect," C. L. Tang and
H. Statz, Appl. Phys. Letters 10, 145 (1967).

This research is supported by the Advanced Research Projects Agency
and the Office of Naval Research

THEORETICAL STUDIES OF THE DYNAMIC AND NON-LINEAR PROPERTIES OF LASER SYSTEMS

C. L. Tang, Associate Professor, Department of Electrical Engineering

Objective

To work out detailed theories for various dynamic and non-linear properties of different laser systems.

Approach

Solve the appropriate density matrix equations and Maxwell's equations.

Progress

A detailed theory has been worked out which explains various aspects of the recently observed phase-locking phenomena in lasers. When a large number of simultaneously oscillating laser modes are locked together, extremely sharp ($\lesssim 10^{-11}$ sec) and intense light pulses can be generated.

PUBLICATIONS

- "Phase Locking of Laser Oscillators by Injected Signal," C. L. Tang and H. Statz, J. Appl. Phys. 38, 323 (1967).
- "Effects of Anomalous Dispersion on the Mode Shapes of Fabry-Perot Oscillators," C. L. Tang, J. Appl. Phys. 38, 886 (1967).
- "Self-Locking of Modes in Lasers," H. Statz, G. deMars, and C. L. Tang, J. Appl. Phys. 38, 2212 (1967).
- "The Maximum Emission Principle and Phase Locking of Modes in Lasers," C. L. Tang and H. Statz, J. Appl. Phys. (in press).

STIMULATED BRILLOUIN EFFECT

C.L. Tang, Associate Professor, Department of Electrical Engineering

J. Walder and T. Giallorenzi Research Assistants

Objective

To determine the characteristics of the stimulated Brillouin process in various non-focusing liquids and crystals.

Approach

To make detailed measurements of the characteristics of the Stokes light and the hypersonic wave generated by the stimulated Brillouin scattering of ruby laser light in various non-focusing liquids and crystals.

Progress

Stimulated Brillouin scattering of collimated ruby laser beams in such non-focusing liquids as n-hexane, methanol, and carbon tetrachloride was investigated. It was found that the experimental data agree well with the calculated results obtained on the basis of a simple steady state theory.

PUBLICATIONS

"Characteristics of the Stokes Emission in the Stimulated Brillouin Process," C. L. Tang, J. Appl. Phys. 37, 2945 (1966).

"Stimulated Brillouin Scattering in Non-Focusing Liquids," J. Walder and C. L. Tang, Phys. Rev., 155, 318 (1967).

This research is supported by the Air Force Cambridge Research Laboratory and the Rome Air Development Center

LATTICE AND CHEMICAL DEFECTS IN FLUORITE CRYSTALS

A. Taylor, Assistant Professor, Department of Materials Science
and Engineering

E. Barsis and M. Baker Research Assistants

Objective

To investigate dielectric and anelastic loss peaks associated with impurity-interstitial F^- complexes; to continue to study the nature of diffusion on the cation sublattices, and to investigate the nature of the interaction between lattice defects and dislocations.

Approach

Dielectric, conductivity, internal friction, mechanical deformation studies.

Progress

A study of the ionic conductivity vs. temperature of the BaF_2 doped with GdF_3 , NaF and BaO has lead to the following principle results: dominant lattice disorder-Frenkel anion, site of Gd^{+++} , substitutional, site of Na^+ interstitial, mobility fluorine vacancy

$\frac{6.4 \times 10^2}{T} \exp\left(\frac{-0.56 \pm 0.03}{kT}\right) \text{ cm}^2/\text{volt sec}$, and mobility fluorine

interstitial $\frac{4 \times 10^3}{T} \exp\left(\frac{-0.79 \pm 0.03}{kT}\right) \text{ cm}^2/\text{volt sec}$. These results

indicate that relaxation mechanisms assigned to anelastic and dielectric loss peaks are incorrect and further work is required. The diffusion of cations, host or dopant, is orders of magnitude smaller than the fluorine defect diffusion and is largely structure sensitive.

PUBLICATIONS

"Ionic Conductivity of MgF_2 Doped LiF ," E. Barsis, E. Lilley and A. Taylor, Ceramic Proceedings 9, 1966.

"The Behavior of Point Defects in Some Fluorite Crystals," E. H. Barsis, Ph.D. Thesis Cornell University, June 1967.

This research is supported by the Advanced Research Projects Agency

DYNAMITRON PROJECT

A. Taylor, Assistant Professor, Department of Materials Science
and Engineering

P. Hanley Research Assistant

Objective

To study radiation damage in ionic crystals using mono-energetic neutrons. Construction of necessary beam transport and targeting equipment.

Approach

Research and development of beam transport systems for high power ion beams in the MeV energy range.

Progress

Beam handling and target system capable of handling greater than 10 kw beams has been completed. Investigations of relaxation spectrum caused by neutron irradiation damage is in progress.

PUBLICATIONS

"Water Cooled Target for Intense Ion Beams," P. R. Hanley, A. W. Haberl, and A. Taylor, Proceeding of the 1967 U. S. Particle Accelerators Conference, March, Washington, D. C.

This research is supported by the Atomic Energy Commission and the Advanced Research Project Agency

CRITICAL AND COOPERATIVE PHENOMENA, DEFECTS AND IDEAL CRYSTALS

W. W. Webb, Professor, Department of Engineering Physics

J. W. Schwartz Research Associate

S. Burns, W. Gilmore, J. Huang and P. Scesney Research Assistants

Objective

(1) Analyze the brittle-plastic transition in the fracture of semiplastic ideal crystals and in glass and understand the plastic flow of ice.

(2) Study the interface between near critical fluids and mixtures, including quantum fluids, in equilibrium.

(3) Study the time dependence of long range correlations in dilute fluids.

Approach

(1) Dynamics of fracture propagation has been measured using high speed photography, thermal stress and other special techniques.

(2) Critical interfaces and correlations in fluids are being studied by optical methods including scattering, spectral analysis and interferometry.

Progress

Experiments on fracture, including dynamic measurements of cleavage surface energy, analyses of the brittle-plastic transition and on the internal fracture of glass were completed and are being analyzed.

Measurements of the thickness and estimate of the profile of the interface between two critical fluids in equilibrium were completed and assembly of apparatus to study time dependent correlations in dilute fluids and interfaces in cryogenic fluids was started.

PUBLICATIONS

"Photoelastic Observations of Transient Heat Transfer Across a Solid-Fluid Boundary," C. Y. King and W. W. Webb, J. Heat Transfer 89, 65 (1967).

"Dislocations and Plastic Deformation of Ice," W. W. Webb and C. E. Hayes, Phil. Mag. (in press).

This research is supported by the Advanced Research Projects Agency and the National Science Foundation

HARD SUPERCONDUCTING MATERIALS

W. W. Webb, Professor, Department of Engineering Physics

R. Labusch Research Associate

M. Beasley, R. Brand, W. Fietz, A. Rueda and R. Warburton
Research Assistants

Objective

To understand properties of superconductors involved in current conduction at high current densities in high magnetic fields.

Approach

Flux creep, critical currents and magnetization, trapped flux, flux flow and other properties subject to hysteresis in superconductors of known defect structure are measured and analyzed.

Progress

During this year studies of (1) the temperature dependence of the generalized Ginzburg-Landau parameters κ_1 and κ_2 , (2) the effect of heavy plastic deformation on the field and temperature dependence of the critical current densities of alloys, and the effects of plastic deformation on the pressure dependence of the critical temperatures of thallium were completed. The work on the temperature dependence of κ_1 and κ_2 showed that the temperature dependence is much larger than predicted by existing theory for all values of electron mean free path and suggested that the theoretical difficulty lies not in the description of the superconducting state but rather in the description of the electronic structure of the normal metal. The work on critical current densities provides a detailed quantitative characterization of the interaction of dislocations with the fluxoid array in type II superconductors where this interaction can lead to enormous increases of critical current densities. These results are still being analyzed.

Dr. K. Labusch has recently completed a formulation of the Ginzburg-Landau equations that includes elasticity effects. His results substantiate our earlier estimate of the strength of the interaction of an individual fluxoid with a dislocation. Currently a study of flux creep in plastically deformed type II superconductors using a superconducting quantum interferometer is adding to our understanding of pinning effects. The picture that is emerging largely confirms the general ideas of the critical state as a condition in which the rate of thermally activated creep or motion in the fluxoid array becomes negligible. However, it has the interesting feature that the dominant temperature dependence of the properties of the state arise from the temperature dependence of the basic superconducting properties and not directly from an Arrhenius factor as has often been suggested.

W. W. Webb

PUBLICATIONS

"Analysis of a Superconducting Solenoid and of Flux Flow Velocity Using an NMR Field Probe," R. F. Engle, M.S. Thesis, September 1966.

"Mechanisms Determining Critical Magnetization Current Densities in Cold Worked Type II Superconductors," W. W. Webb and W. A. Fietz, Proc. Tenth Int. Conf. on Low Temperature Physics, Moscow, 1966.

"Increase of the Anisotropy of the Energy Gap in Superconducting Thallium Under Pressure," W. Gey, Phys. Rev. 153, 422 (1967).

"Influence of Lattice Structure on Superconductivity in Thallium," W. Gey, Sol. State Comm. 4, 402 (1966).

"Magnetic Properties of Some Type II Alloy Superconductors Near the Upper Critical Field," W. A. Fietz and W. W. Webb, Phys. Rev. (in press).

This research is supported by the Atomic Energy Commission

PLAIT POINTS IN TERNARY SYSTEMS

B. Widom, Professor, Department of Chemistry

J. Zollweg Research Assistant

Objective

Experimental characterization of Plait points.

Approach

Observation of compositions of isothermal phase separation, and determination of coherence lengths of composition fluctuations.

Progress

The determination of the isothermal phase separation compositions is far along and should be completed within the next few months, after arrival of temperature and purity control instruments. The second half of the experimental program, on coherence lengths, has not yet begun.

PUBLICATIONS

"Plait Points in Two- and Three-Component Liquid Mixtures," B. Widom, J. Chem. Phys. 46, 3324 (1967).

" 'Hard Core' Model of Liquids," N. S. Snider, J. Chem. Phys. 45, 378 (1966).

"A Non-Combinatorial Method for Determining the Entropy of Lattices," G. W. Woodbury, J. Chem. Phys. 47, 270 (1967).

"Intermolecular Forces and the Nature of the Liquid State," B. Widom, Pontif. Acad. Sci. Scripta Varia n. 31 [reprinted in Science 157, 375 (1967).]

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"Extensions of the Widom Model for Two- and Three-Component Liquid Mixtures," G. Neece, J. Chem. Phys. (in press).

This research is supported by the Advanced Research Projects Agency and the Office of Saline Water

QUASIPARTICLE SELF ENERGY OF A FERMI LIQUID AND THE SPECIFIC HEAT OF He^3

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Research Associates

Objective

To examine the effect of density and spin fluctuations on the quasiparticle self energy of a Fermi liquid. Knowledge of the self energy leads to modification of the specific heat predicted previously by the Landau theory.

Approach

The investigations of the modification of the quasiparticle self energy and the specific heat of He^3 are being carried out entirely within the context of the microscopic theory of a normal Fermi liquid.

Progress

When the results of this work are applied to the problem of the specific heat of liquid He^3 it is found that the specific heat has a form

$$C_V = aT + bT^3 \log \frac{T}{T_b} + cT^5 \log \frac{T}{T_c}$$

The complete analytic form of b , the first correction, in terms of Fermi liquid parameters is now known. Calculation of c apparently cannot be done within the theory as presently formulated. With a and T_b as parameters, the comparison between theory and experiment is quite satisfactory.

PUBLICATIONS

"Quasiparticle Self energy and Specific Heat of a Fermi Liquid: Application to He^3 ," D. J. Amit, J. W. Kane and H. Wagner, Phys. Rev. Letters 19, 425 (1967).

This research is supported by the Advanced Research Projects Agency, the Office of Naval Research and the National Science Foundation

PROPERTIES OF DILUTE MAGNETIC ALLOYS

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D. Langreth Research Associate

Objective

To investigate the properties of dilute magnetic alloys.

Approach

Special attention is paid to what can be learned about localized magnetic moments by electron spin resonance. Of particular interest is the effect of the Kondo anomaly on resonant line positions and widths, and whether the Kondo shift can be "bottlenecked" in the same way as the mean field shifts. The effect of the hyperfine interaction in the solute is also under investigation.

Progress

A set of Bloch-like equations to describe resonance in a system with a strong s-d interaction have been derived from first principles. These equations include the effects of the Kondo anomaly, mean field shifts, as well as the hyperfine interaction. The equations predict that the Kondo shift is easily "bottlenecked", in contrast with earlier speculations of others. Its effect might be seen, however, as a modulation of the hyperfine interaction at low temperatures.

This research is supported by the Advanced Research Projects Agency

ATOMIC GAS LASER SPECTROSCOPY

G. J. Wolga, Associate Professor, Department of Electrical Engineering

T. Carroll, T. Johnston, and R. Abrams Research Assistants

Objective

To study the interaction of atoms and radiation in lasting atomic systems. The combined effects of optical, microwave and d.c. magnetic fields on laser action are studied. Spectroscopic properties of excited atomic states are studied. Collision processes in excited atomic states are studied. To extend the theory of the laser to operation with the addition of external fields.

Approach

Laser oscillators or amplifiers subjected to combined external fields are studied by observing changes in laser power and/or absorption of microwave power as a function of operating conditions. Atomic collisions are studied by modulating the laser power and observing synchronously modulated spontaneous emission from several states arising from collisional excitation transfer.

Progress

An experimental and theoretical study of double resonance effects in a Zeeman laser at 1.52μ has been completed. Three level effects related to the coupling of three discrete atomic levels by laser fields are being completed. The $^3P_2$ - $^3P_4$ fine structure separation in Neon has been measured. Energy transfer by atomic collisions and collision cross sections in excited states of Helium are being studied in a near infrared He laser.

PUBLICATIONS

"Double Resonance Gas Laser Spectroscopy in Neon," T. O. Carroll and G. J. Wolga, IEEE Jrl. of Quantum Electronics QE-2, 9, 456 (1966).

"Laser Pumped Microwave Emission in Excited States of Neon," T. F. Johnston, Jr. and G. J. Wolga, IEEE Jrl. of Quantum Electronics QE-2, 9, 412 (1966).

"Near Infrared Laser Oscillations in Pure Helium," R. Abrams and G. J. Wolga, IEEE Jrl. of Quantum Electronics, August (1967).

This research is supported by the Advanced Research Projects Agency

INVESTIGATION OF COHERENCE OF Q-SWITCHED RUBY LASER EMISSION

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A. Flamholz Research Assistant

Objective

To study the coherence of Q-switched ruby laser emission and non-linear optical processes. To study the changes in the optical properties of the laser medium resulting from the depletion of population inversion during the emission process.

Approach

The time coherence or variation of emission frequency with time is studied with a two pinhole interferometer. One pinhole is directly illuminated while the other is illuminated after a controlled time delay. The fringe visibility and fringe movement are observed with a time resolved detector system. Fringe movement is correlated with change of laser frequency with time during emission. The change in frequency is related to changes in optical properties of the laser medium.

Progress

The spectral purity and mode properties of the Q-switched laser were significantly improved. Data has been obtained for the Q-switched laser. Final runs with improved temporal resolving power indicate excellent agreement with previous work with the non-Q-switched ruby laser. Subsequently, a stimulated, non-linear optical process will be studied.

PUBLICATIONS

"Transient Interference Studies of Emission from a Pulsed Ruby Laser,"
D. A. Berkley and G. J. Wolga, J. Appl. Phys. July (1967).

"Properties of a Single Mode Passive Q-switched Ruby Laser," A.
Flamholz, M.S. Thesis, September 1966.

This research is supported by the United States Air Force

MOLECULAR LASER RESEARCH

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T. Carroll and S. Marcus Research Associates

N. Djeu, T. Kan, C. Miller and H. Powell Research Assistants

Objective

To study the spectroscopic properties of excited molecular states that are relevant to lasing. To study relaxation and excitation processes in molecular systems. To employ the high laser power that is available to induce and study non-linear optical processes.

Approach

Gain and power saturation measurements on individual rotation-vibration transitions are being made. The saturation process of the molecular oscillation is also being studied via the Lamb dip. Triple quantum transitions stimulated by molecular laser power are being studied. The spontaneous emission from excited molecular states is being studied to reveal excitation transfer and relaxation.

Progress

Frequency selective molecular lasers have been constructed and operated. The available power supply for gas excitation is being modified for higher voltage operation. Saturation studies and gain measurements in $\text{CO}_2\text{-He-N}_2$ and work on triple quantum transitions have been initiated. Similar studies of the $\text{N}_2\text{O-N}_2\text{-He}$ laser are underway.

PUBLICATIONS

"Work Function Estimation with a Single Yield Measurement," M. C. Teich and G. J. Wolga, J. Opt. Soc. Am. 57, 542 (1967).

"Volume Intraband Photoelectric Effect," H. C. Bowers and G. J. Wolga, Phys. Rev. (in press).

This research is supported by the Office of Naval Research

THE APPLICATION OF $\text{Sn}^{119\text{m}}$ MÖSSBAUER SPECTROSCOPY TO CHEMICAL PROBLEMS

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E. W. Randall

Research Associate

N. W. G. Debye, E. Rosenberg, S. E. Ulrich, C. M. Silcox Yoder and
J. G. Zavistoski Research Assistants

Objective

To explore the application of $\text{Sn}^{119\text{m}}$ Mössbauer spectroscopy to chemical problems.

Approach

1) To subject the current hypothesis for the connection between the measureable parameters in Mössbauer spectroscopy and chemical behavior to experimental test; 2) To apply the technique to the analysis of tin-bearing mineralogical samples for structure and valency; 3) To apply the technique as a routine adjunct to synthetic inorganic chemistry; 4) To apply the technique to elucidate the nature of the bonding in tin systems.

Progress

The hypothesis of a linear correlation between Mössbauer Isomer Shift and the ionic character of the bonds connected to tin has been tested; a dozen different tin minerals have been examined; it has been shown that the technique can be used as a routine adjunct to our synthetic chemistry; data to support the suggestion of (d $\rightarrow$ d)- π bonding in certain tin-cobalt systems has been derived.

PUBLICATIONS

"Donor-Acceptor Complexes of Bis(o-phenylene diory) Silane and Germane", C. M. Silcox Yoder and J. J. Zuckerman, Inorg. Chem. 6, 163 (1967).

"Methyl-Tin Bond Cleavage by an Organolithium Reagent. A Routine Use of $\text{Sn}^{119\text{m}}$ Mössbauer Spectroscopy as an Adjunct to Synthetic Chemistry", J. G. Zavistoski and J. J. Zuckerman, Inorg. Chem. (Accepted for Publication).

"The Application of $\text{Sn}^{119\text{m}}$ Mössbauer Spectroscopy to Chemical Problems", J. J. Zuckerman, Mössbauer Effect Methodology, Vol. III, (In Press).

J. J. Zuckerman

" $\text{Sn}^{119\text{m}}$ Mössbauer Spectra of Tin-Containing Minerals", J. J. Zuckerman
and D. L. Smith, J. Inorg. Nucl. Chem. (In Press).

"Chemical Significance of Mössbauer Spectral Parameters. $\text{Sn}^{119\text{m}}$
Isomer Shift and Percentage Ionic Character of Tin Bonds",
J. Inorg. Nucl. Chem. (In Press).

This research is supported by the Advanced Research Projects Agency
and the National Science Foundation

ELIMINATION OF SOME PROPOSED STRUCTURES FOR THE GRIGNARD REAGENT

J. J. Zuckerman, Assistant Professor, Department of Chemistry

E. W. Randall

Research Associate

Objective

To eliminate some structures proposed for the CH_3MgI Grignard Dimer.

Approach

To synthesize $\text{H}_2\text{C}^{13}\text{-MgX}$ and measure the $\text{C}^{13}\text{-H}^1$ spin-spin coupling constant in various concentrations and at various temperatures where the reagent is known to be a dimer. We assume that $J(\text{C}^{13}\text{-Mg-C-H}^1)$ is observable, i.e., > 2 cps.

Progress

The results allow elimination of any of the proposed structures which contain two methyl groups on a single magnesium in a static system.

This research is supported by the Advanced Research Projects Agency and the National Science Foundation

SYNTHESIS AND STUDY OF GROUP IV-OXYGEN HETEROCYCLES AND THEIR DERIVATIVES

J. J. Zuckerman, Assistant Professor, Department of Chemistry

E. W. Randall Research Associate

C. M. Silcox Yoder Research Assistant

Objective

The preparation of a series of Group IV-Oxygen ring compounds which vary in a monotonic way in some property.

Approach

To synthesize a series of 5, 6 and 7 membered ring compounds incorporating carbon, two oxygen atoms and carbon, silicon, germanium and tin in A - O - M - O arrangements.

Progress

Over 35 such systems have been prepared and studied by infrared, NMR and Mössbauer techniques.

PUBLICATIONS

"The Role of $\nu(\text{C-N})$ as Evidence for the Mode of Binding of Amides to Lewis Acids," E. W. Randall, C. M. Silcox Yoder and J. J. Zuckerman, *Inorg. Chem.* 5, 2240 (1966).

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"Benzodioxles, Naphthodioxins, and Dibenzodioxepins," C. M. Silcox Yoder and J. J. Zuckerman, *J. Heterocyclic Chem.* 4, 166 (1967).

This research is supported by the Advanced Research Projects Agency and the National Institutes of Health

AMINATION AND TRANSAMINATION AS ROUTES TO FOURTH GROUP GEM-DIAMINES

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C. H. Yoder Research Assistant

Objective

To investigate homologous series of fourth group gem-diamines, both linear and cyclic, monomeric and polymeric.

Approach

To employ amination and transamination in a systematic way to synthesize the above named systems, and to employ NMR and IR spectroscopic techniques to study them.

Progress

Series of gem-diamines of carbon, silicon, germanium and tin, linear and cyclic, monomeric and polymeric have been prepared and characterized. Several trends in physical chemical and spectroscopic properties have been observed and their significance interpreted. For example, in amination of $(CH_3)_2MCl_2$ by $(C_2H_5)_2NH$ $Si > Ge > Sn$ but in transamination of the resulting $(CH_3)_2M[N(C_2H_5)_2]_2$ $Si < Ge < Sn$

PUBLICATIONS

- "Transmission of Substituent Effects Through the N-Si-N-System," C. H. Yoder and J. J. Zuckerman, *Inorg. Chem.* 6, 103 (1967).
- "Infrared Spectra of Group IV gem-Diamines," C. H. Yoder and J. J. Zuckerman, *Inorg. Chem.* 5, 2055 (1966).
- "Amination and Transamination as Routes to Fourth Group Diamines," C. H. Yoder and J. J. Zuckerman, *J. Am. Chem. Soc.* 88, 4831 (1966).
- "Group IV Imidadizolidine Expansion-Contraction Reactions," C. H. Yoder and J. J. Zuckerman, *Chem. Commun.* 694 (1966).
- "N.M.R. Studies of Exchange in Stanylamines," E. W. Randall, C. H. Yoder and J. J. Zuckerman, *J. Am. Chem. Soc.* 89, 3438 (1967).
- "Proton Magnetic Resonance and Basicity Studies of Linear and Cyclic gem-Diamine Derivatives of Elements in Group IV," E. W. Randall, C. H. Yoder and J. J. Zuckerman, *Inorg. Chem.* 6, 744 (1967).

This research is supported by the National Institutes of Health and the National Science Foundation

THE ELUSIVE ($p \longrightarrow d$)- π BOND

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E. W. Randall Research Associate

C. H. Yoder Research Assistant

Objective

To elucidate the nature of the bonds silicon and the lower members of the fourth group make with atoms holding lone pair electrons (as in the case of nitrogen) or with systems with π -electrons (as in the case of the phenyl-ring).

Approach

By study of i) the transmission of information through the N-Si-N system; ii) the N^{15} - H^1 spin-spin coupling constants in the NMR as a guide to nitrogen hybridization in these systems; (iii) the acid strengths of p-substituted benzoic acids and phenols as a guide to the electrical effect of the trimethylsilyl group.

Progress

The results of these experiments have led to an agnostic view toward large ($p \longrightarrow d$)- π contributions to these bonds. (1) there seems little difference between the N-Si-N and N-C-N systems; (2) the hybridization at nitrogen as measured by $J(N^{15}-H^1)$ changes in a way opposite to that expected on the basis of ($p \longrightarrow d$)- π bonding; (3) the strengths of the substituted benzoic acids are those expected on the basis of electronegativity differences between H, C and Si.

PUBLICATIONS

"The Elusive ($p \longrightarrow d$)- π Bond," E. W. Randall and J. J. Zuckerman, Chem. Commun. 732 (1966).

"Transmission of Substituent Effects Through the N-Si-N System," C. H. Yoder and J. J. Zuckerman, Inorg. Chem. 6, 103 (1967).

This research is supported by the National Science Foundation

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